^{14}C u okolišu
^{14}C v okolju
^{14}C in environment

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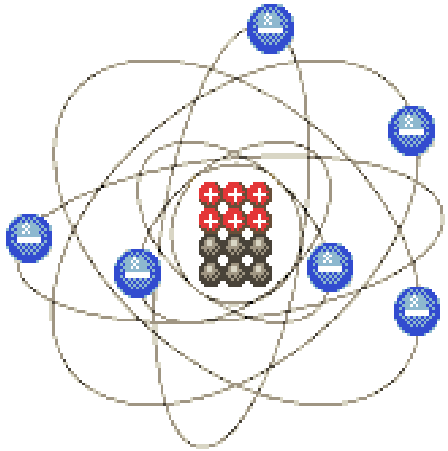
IJS, Ljubljana, 9.12.2015.

- ^{14}C metoda – uvod, ciklus ugljika, produkcija ^{14}C
- Raspodjela ugljika u prirodi (atmosfera)
- Određivanje starosti
- Veličine i jedinice
- Procjena doze
- Mjerne tehnike određivanja ^{14}C
- Monitoring ^{14}C u okolici NE
- Monitoring u okolici NEK

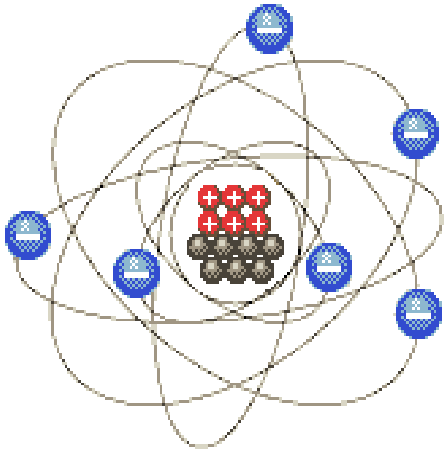
Carbon isotopes



^{12}C

98.89 %

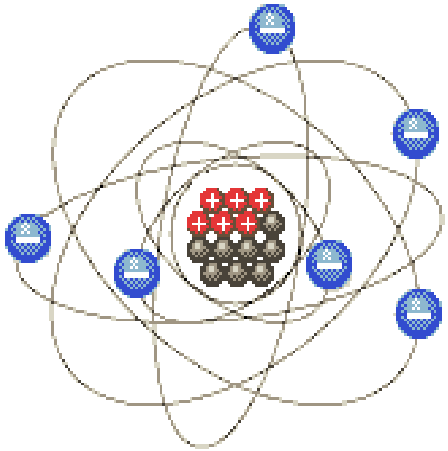
p = n = 6



^{13}C

1.11 %

n = 7



^{14}C

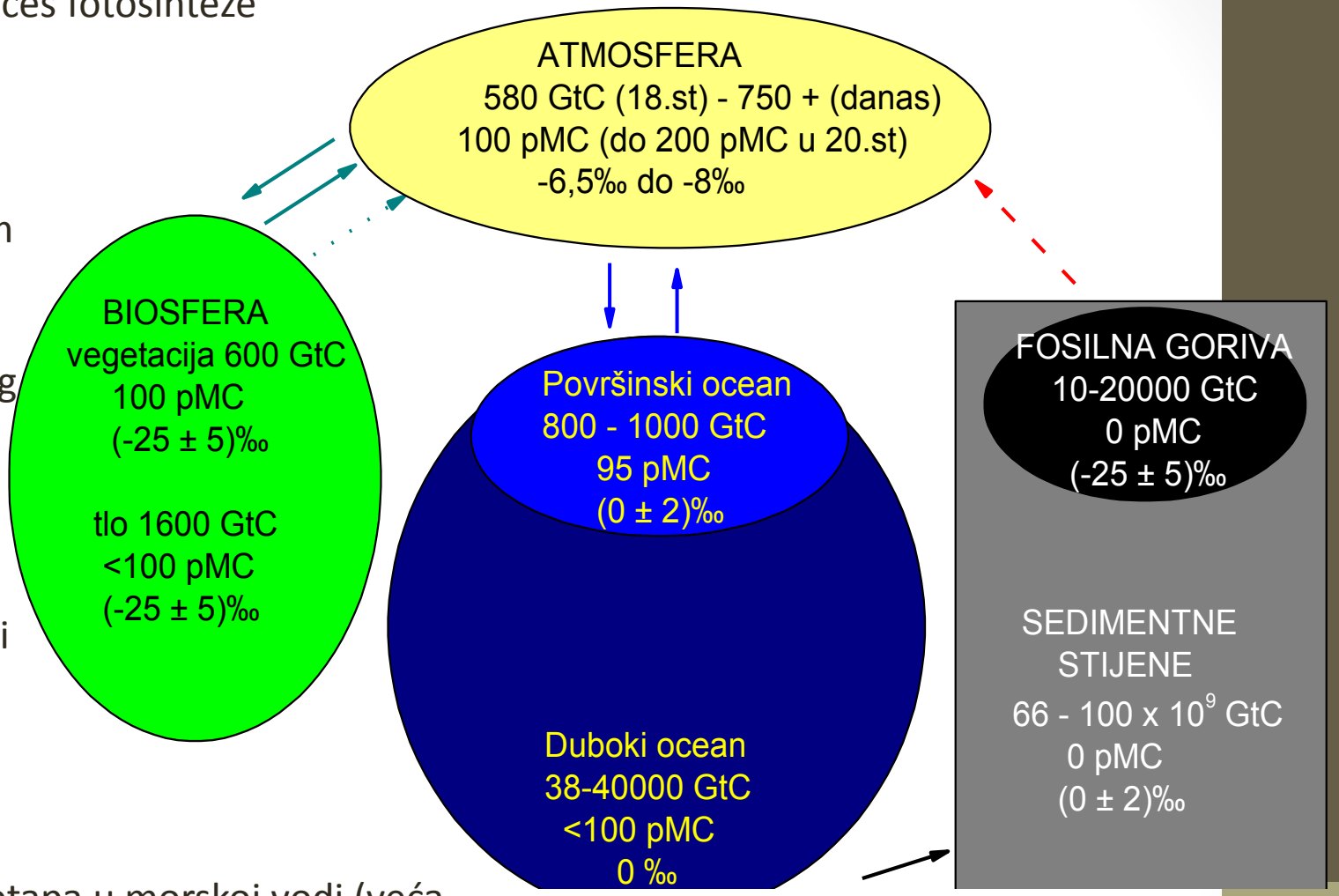
10^{-10} %

n = 8

$T_{1/2}$ = 5730 y

U atmosferi - uglavnom kao CO_2, 0,03 (0,04)% vol. - važna uloga za održavanje života na Zemlji - koriste biljke za proces fotosinteze

Vraća se u atmosferu disanjem biljaka i životinja, raspadanjem biljnog i životinjskog tkiva, spaljivanjem organskog materijala, oslobađanjem iz tople morske vode i vulkanskim erupcijama.



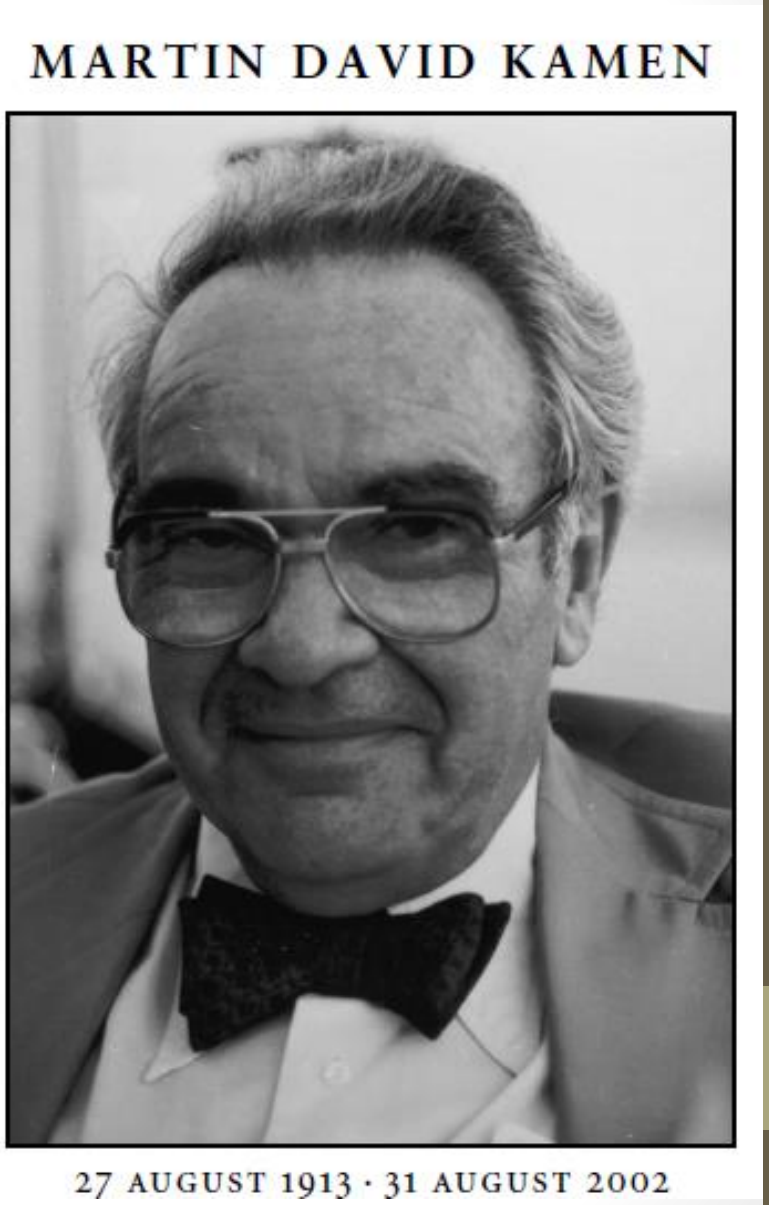
CO_2 se otapa u morskoj vodi (veća topivost u hladnijoj vodi), a i u vodi koja prolazi kroz tlo, stvarajući ugljičnu kiselinu, koja može otapati vapnenačke stijene.

Izgaranjem fosilnih goriva oslobađa se ugljik koji je milijunima godina bio spremljen u litosferi.

Discovery of ^{14}C

Obituary
Martin Kamen
Scientist, co-discoverer of the isotope that gave archaeology carbon-dating, and innocent victim of America's Communist witchhunts
(Pearce Wright , The Guardian,
Monday 9 September 2002)

The American scientist Professor Martin Kamen was the co-discoverer of the radioactive isotope carbon-14. The finding transformed biochemistry as a tracer following chemical processes in plants, while its use in the carbon dating of fossils and ancient artefacts between 500 and 50,000 years old revolutionised archaeology.



Science 10 May 1963:
Vol. 140 no. 3567 pp. 584-590
DOI: 10.1126/science.140.3567.584

Sam Ruben and Martin Kamen co-discovered the isotope carbon-14 on February 27, 1940, at the University of California Radiation Laboratory, Berkeley, when they bombarded graphite in the cyclotron in hopes of producing a radioactive isotope of carbon that could be used as a tracer in investigating chemical reactions in photosynthesis. Their experiment resulted in production of carbon-14.

Ruben S, Kamen MD (1940)
Radioactive carbon of long-half life.
Phys. Rev. 57: 549

Martin Kamen, has been named one of two winners of this year's (1995) Enrico Fermi Award. The 82-year old Kamen is joined by 83-year-old physicist Ugo Fano, who won for his pioneering contributions to the theory of atomic and radiation physics.

Early History of Carbon-14

Discovery of this supremely important tracer was expected in the physical sense but not in the chemical sense.

Martin D. Kamen

When, how, and why was carbon-14 discovered? As T. S. Kuhn has remarked (*1*), discovery is seldom a single event that can be attributed wholly to a particular individual, time, or place. He notes that some discoveries, such as those of the neutrino, radio waves, and missing isotopes or elements, are predictable and present few problems, as far as establishment of priority is concerned. Others, such as the discoveries of oxygen, x-rays, and the electron, are unpredictable. These put the historian in a "bind" when he tries to decide when, how, who, and where the discovery was made. Much more rarely does he have a basis for an answer to the question "Why?"

I propose in this account of the "prenatal" history of carbon-14 to provide the answers to my leading questions (*2*). These make a story which is a fragment of the whole record. That record must be constructed by future historians who seek to probe the events of a period in which there has been an unparalleled impact of intellectual curiosity and scientific creativity on the structure of society.

The tremendous outburst of technology in the past half century, the result of the rise of nuclear science, has crowned man's quest for the philospher's stone so successfully as to be hardly credible even to the most optimistic alchemist. Tracer methodology, an offspring of nuclear science, has provided essential support for the ever-widening and deepening knowledge of structure and function in biological systems, expressed as the dynamic science of molecular biology.

These developments have profound, but unknown, implications for the future of our social structures. They obviously bring with them an unexampled load of grist for the mills of cultural historians, social scientists, and philosophers. Perhaps the novelists will dig into the record of these exciting times for fresh insights into the age-old drives of mankind.

Carbon-14, the long-lived carbon isotope, is the most important single tool made available by tracer methodology, because carbon occupies the central position in the chemistry of biological systems. Thus it plays, and will continue to play, an essential role in the elucidation of biochemical mechanisms, knowledge of which is essential in the further development of molecular biology. Obviously, the circumstances surrounding its discovery are valid objects of interest for the historian (*3*).

Initial Phases, 1934–36

In the early 1930's, nuclear physics, immersed in the great traditions of the Cambridge school led by Ernest Rutherford, was concerned primarily with observations of processes associated with the scattering of elementary nuclear particles by various atomic nuclei. Reports in those times show painstaking determinations of range-energy relations for the fundamental projectiles (protons, deuterons, alpha particles). The energies used did not exceed approximately 10 Mev, because of the limitations set by the relatively primitive accelerators and by the radiation characteristics of the naturally radioactive materials that were available. The rationale for such work, which often involved tedious attention to detail and much labor, was that if enough precise facts were put together, accurate binding energies for nuclei could be deduced. From these energies, it was reasoned, there could be derived a solid basis for further attack on the problem of the nature of nuclear forces.

By 1933, such data—binding energies, angular distributions in scattering experiments, and so on—had demonstrated that nuclear forces could be described as analogous to saturation exchange forces like those postulated previously for chemical bonding. The so-called "alpha-particle" model of the nucleus already contained the seeds of what was to be the full-fledged modern "shell" theory of nuclei, to be developed later by Maria Mayer, Eugene Feenberg, and others.

As to my part in this, I was a young, eager student and had just begun doctoral research, using the Wilson cloud chamber to study the angular distribution of neutrons scattered in collisions with protons and other nuclei. These researches were part of a general program initiated in the laboratory of W. D. Harkins in the chemistry department at the University of Chicago (*4*). My decision to work in this field was largely a result of the influence of D. M. Gans, Harkins' associate and an assistant professor in the department (*5*).

Most significantly for this history, similar work was also under way at Yale, where F. N. D. Kurie, investigating neutron-induced disintegration of light elements, had obtained certain anomalous results for the angular distributions of protons in collisions with neutrons. In 1934 he proposed a radical interpretation (*6*) of certain events he noted in the cloud chamber. When nitrogen was exposed to fast neutrons, for instance, he noted that in some cases the ejected nucleus produced a very long, thin track. This he ascribed to a proton, rather than to an alpha particle. Thus, he supposed that the usual reaction, $N^{14}(n,He^4)B^{11}$, was accompanied by a less frequent but readily observable reaction, $N^{14}(n,H^1)C^{14}$. (As far as I am aware, this is the first suggestion in the literature that C^{14} might exist.) Kurie also suggested, however, that the tracks he was observing might arise from H^2, or even H^3, and thus that the reactions $N^{14}(n,H^2)C^{13}$ and $N^{14}(n,H^3)C^{12}$ were also possibilities. In fact, he felt the reactions with emission of H^2 and H^3 were the more likely because they resulted in nuclei of known stability.

The author is professor of chemistry at the School of Science and Engineering, University of California, San Diego. This article is adapted from a paper which he presented at a meeting of the American Chemical Society in Los Angeles in April 1963, when he received the Society's 1963 Award for Nuclear Applications in Chemistry. This paper is also being printed in the May issue of the *Journal of Chemical Education*.

After discovery of radioactive carbon-14, Ruben and Kamen found that it had a half-life of about 5,700 years and that some of the nitrogen in the atmosphere was turned into carbon-14 when hit with cosmic rays. Thus, an equilibrium was reached, the newly formed carbon-14 replacing the carbon-14 that decayed, so that there was always a small amount in the atmosphere.

Ruben S, Kamen MD (1940) Radioactive carbon of long-half life. Phys. Rev. 57: 549

Ruben and Kamen had to abandon attempts to experiment with ^{14}C in 1942.

Willard Libby, a chemist at the University of Chicago, experimented with carbon-14 further. Through a series of tests, he calculated the atom's half-life to be 5,568 years. He theorized that, by analyzing the amount of carbon-14 in plant matter, one could form a solid estimate of the item's age. Namely, he figured that plants would absorb some of this trace carbon-14 while they absorbed ordinary carbon in photosynthesis. Once the plant died, it couldn't absorb any more carbon of any kind, and the carbon-14 it contained would decay at its usual rate without being replaced. **By finding the concentration of carbon-14 left in the remains of a plant, you could calculate the amount of time since the plant had died**. He continued to refine the concept for the next decade, calculating the age of an ancient Egyptian barge using wood samples. The science of archaeology was revolutionized and, for his efforts, Libby received the Nobel Prize in Chemistry for 1960.

Arnold, J.R., Libby, W.F: Age determinations by radiocarbon content: checks with samples of known ages. Science 110 (1949), p.678-680

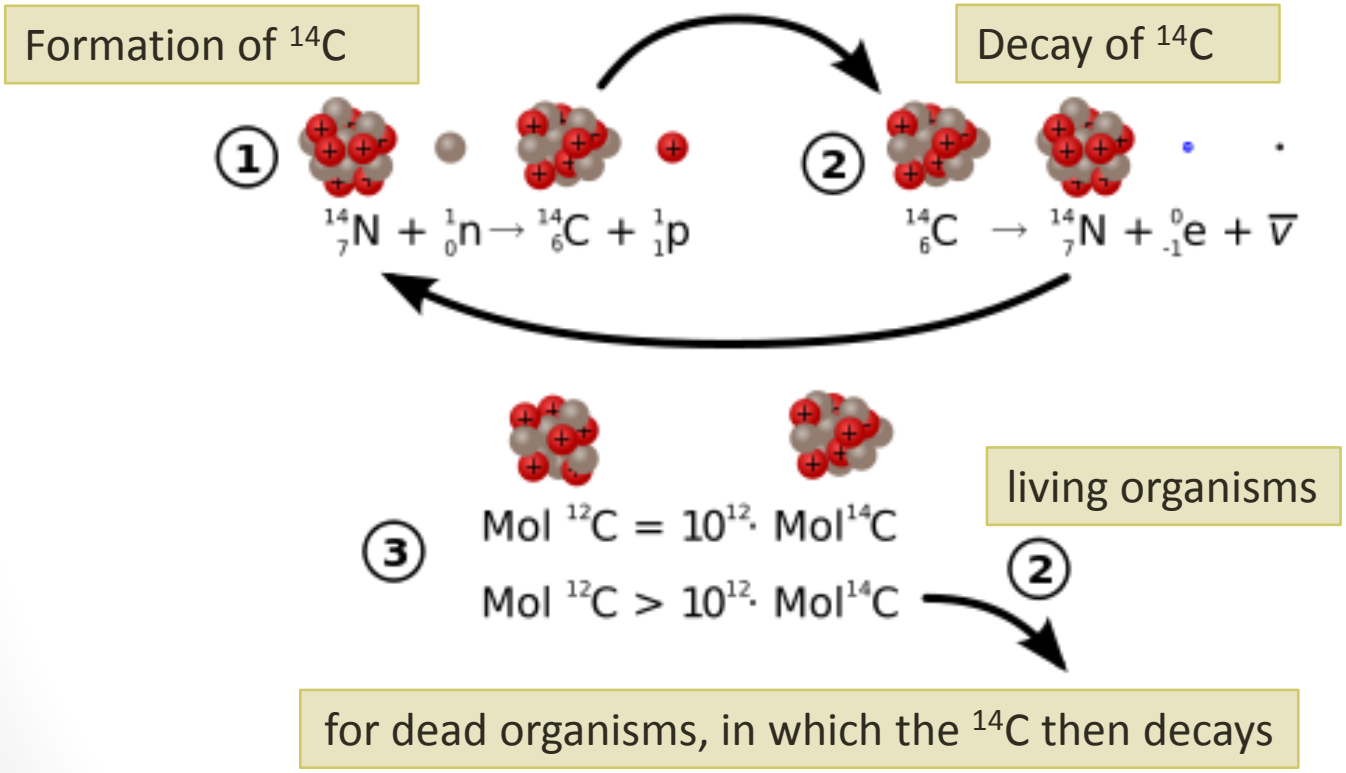
Nastajanje ^{14}C (produkcija)

Kozmogeni i antropogeni izotop/radionuklid

- Prirodno – interakcija neutrona iz kozmičkog zračenja s ^{14}N
- Antropogeno
  - „bomb” ^{14}C
  - nuklearne elektrane
  - drugi nuklearni objekti
- Fosilna goriva – razrjeđenje ^{14}C

Radiocarbon production

Cosmogenic radionuclide - the primary natural source of ^{14}C on Earth is nuclear reaction between neutrons from cosmic rays with nitrogen in the atmosphere (The highest rate of ^{14}C production takes place at altitudes of 9 to 15 km)



Doug McDougall (2008). *Nature's Clocks: How Scientists Measure the Age of Almost Everything*. Berkey & Los Angeles, California: University of California Press. p. 45.

Carbon on Earth

^{12}C: 98.89 %

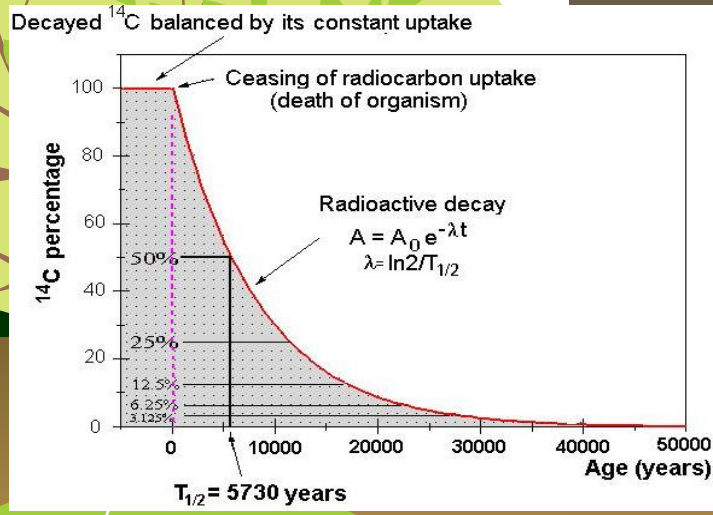
^{13}C: 1.1 %

^{14}C: 1.18 x 10^{-12} %

$$^{14}N + n \rightarrow {}^{14}C + p$$

O_2

$^{14}CO_2$



$$^{14}C \rightarrow {}^{14}N + e + \bar{\nu}$$

Kozmogeni ^{14}C

Produkcija 1.4 - 1.54 PBq/yr – nije jednolika zbog promjenjivog intenziteta kozmičkog zračenja, 11-godišnjeg sunčevog ciklusa, promjene zemljina magnetskog polja ...

U Zemljinoj atmosferi	oko 220 PBq „prirodnog“ ^{14}C
Terestrijalni ^{14}C	oko 10000 PBq

bomb ^{14}C

produced by interactions of neutrons emitted in atmospheric nuclear explosions
input 213 – 315 PBq,
doubled atmospheric specific activity of ^{14}C in 1963,
since then – decrease

^{14}C in nuclear power plants

Minor ^{14}C quantities enter the atmosphere due to nuclear power plants operation

Carbon-14 can be produced by other reactions with neutrons:

- $^{13}C(n,gamma)^{14}C$ and $^{17}O(n,alpha)^{14}C$ with thermal neutrons
- $^{15}N(n,d)^{14}C$ and $^{16}O(n,^{3}He)^{14}C$ with fast neutrons

The most notable routes for ^{14}C production by thermal neutron irradiation of targets (e.g., in a nuclear reactor) are:.

Parent isotope	Natural abundance, %	Cross section for thermal neutron capture	Reaction
^{14}N	99.634	1.81	$^{14}N(n,p)^{14}C$
^{13}C	1.103	0.0009	$^{13}C(n,\gamma)^{14}C$
^{17}O	0.0383	0.235	$^{17}O(n,\alpha)^{14}C$

In PWR ^{14}C is produced by neutron activation with oxygen ^{17}O or nitrogen ^{14}N in fuel, moderator and coolant of the reactor. It is emitted into the environment in the form of **CO_2**, which **enters the natural carbon cycle** in the vicinity of power stations. Through food chain (ingestion) it can contribute to the additional irradiation of the population, resulting thus to the enhancement of the effective dose of the population.

e.g.: Man-Sun Zim and F Caron, Progress in Nuclear Energy 48 (2006) 2-36

Production rate in nuclear facilities

0.3 PBq/yr – estimated global production
(Yim, Progress in Nucl Energy 2006)

gaseous releases

BWR 95% as $^{14}CO_2$, 2.5 % as ^{14}CO, 2.5 % hydrocarbons
PWR – about 80% as $^{14}CH_4$, 20% as $^{14}CO_2$;
Estimated rate of gaseous release 0.5 – 1.9 TBq/GWeyr;
fuel reprocessing plants – gaseous release mostly as $^{14}CO_2$, about 15 TBq/yr;

liquid releases

chemical form of carbonates and various organic compound
relative quantities unknown (IRSN 2010) – others say: mainly as DIC;

example of Sellafield (UK) :
gaseous release 1.5 - 12 E12 Bq, liquid : app. 8 E12 Bq

NEK in 2013: gas 1.3 E11 Bq liquid: 1.7 E9 Bq (REMONT)
NEK in 2014: gas 2.3 E10 Bq 0.8 E9 Bq

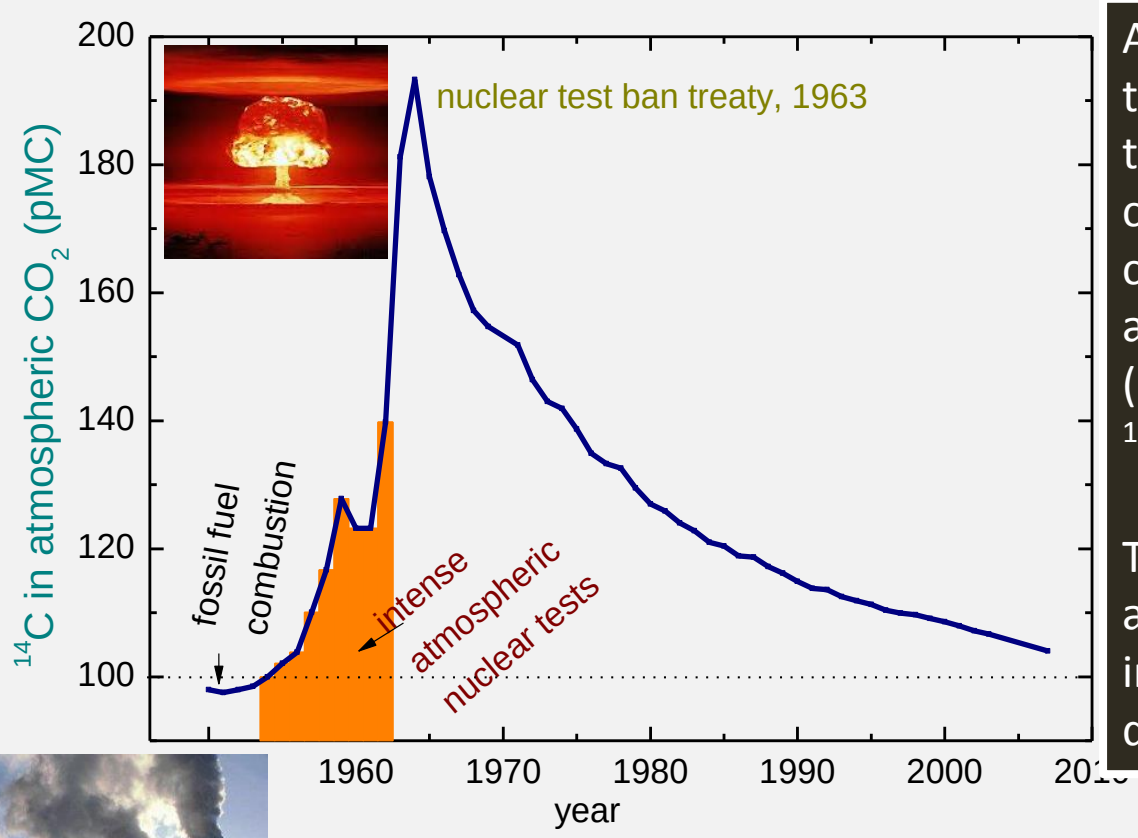
various other sources

(medical and farmaceutical - labelling, industrial) – annual production in the world estimated to 5×10^{13} Bq in 1978, 10×10^{13} Bq in 1987 (all released as $^{14}CO_2$)

fossil fuels

»Suess effect«, increase of pCO_2 in the atmosphere, decrease $\delta^{13}C$

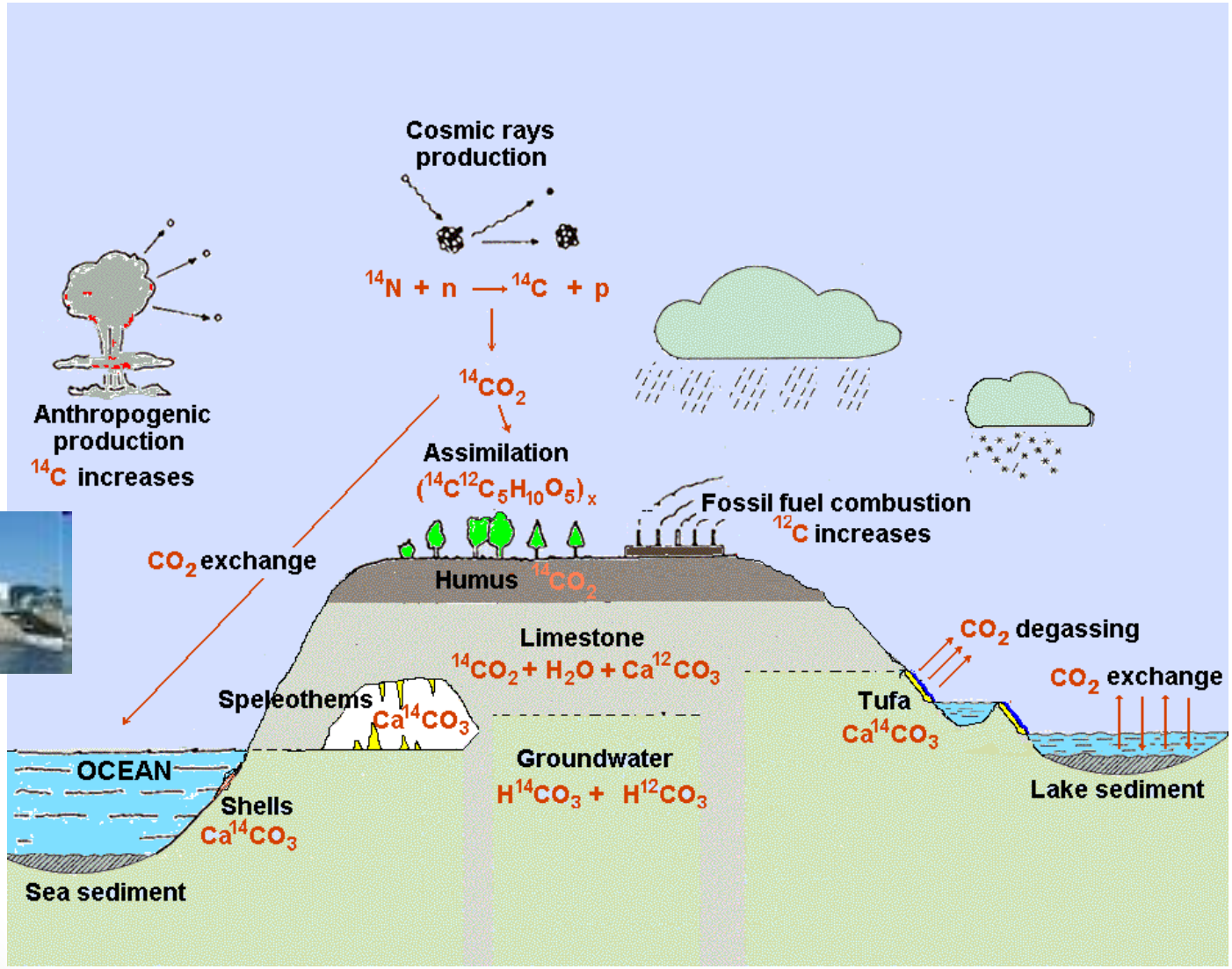
Anthropogenic ^{14}C



Anthropogenic activities disturbed the natural distribution of ^{14}C in the atmosphere through fossil fuel combustion (increasing of ^{12}C compared to ^{14}C)
and atmospheric bomb tests (doubling the natural atmospheric ^{14}C activity in 1960-ties).

The „bomb-peak" has served as an invaluable tracer to get insight into the global carbon cycle on the decadal time scale.

Distribution of ^{14}C

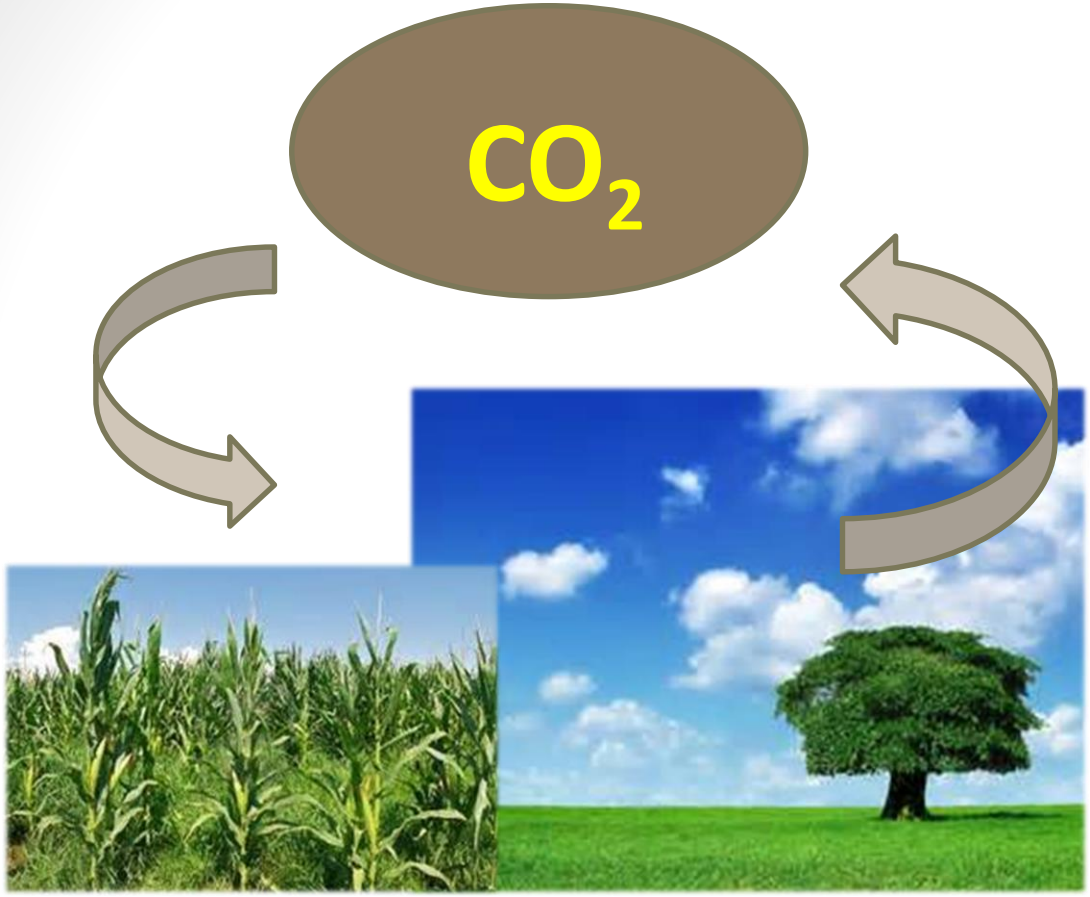


Applications of ^{14}C

- **Dating (determination of age) of organic samples** (wood, grains, leaves/plants, seed, charcoal, leather, textile, linen, bones, teeth, ivory, parchment, paper, antler and horn, peat, soil, organic sediment, dissolved organic carbon…)
- **Dating of secondary carbonates** (inorganic lake sediment, speleothemes, tufa, corals, mollusks, algal rims, dissolved inorganic carbon in water)
- **Carbon cycle in nature** (including atmospheric CO_2)
- **Environmental monitoring** (nuclear facilities)
- Oceanology, climatology
- Forensic science
- Medical biochemical, pharmacological applications
- Determination of biofuel fraction

Carbon cycle - atmosphere

Carbon cycle



Biogenic carbon

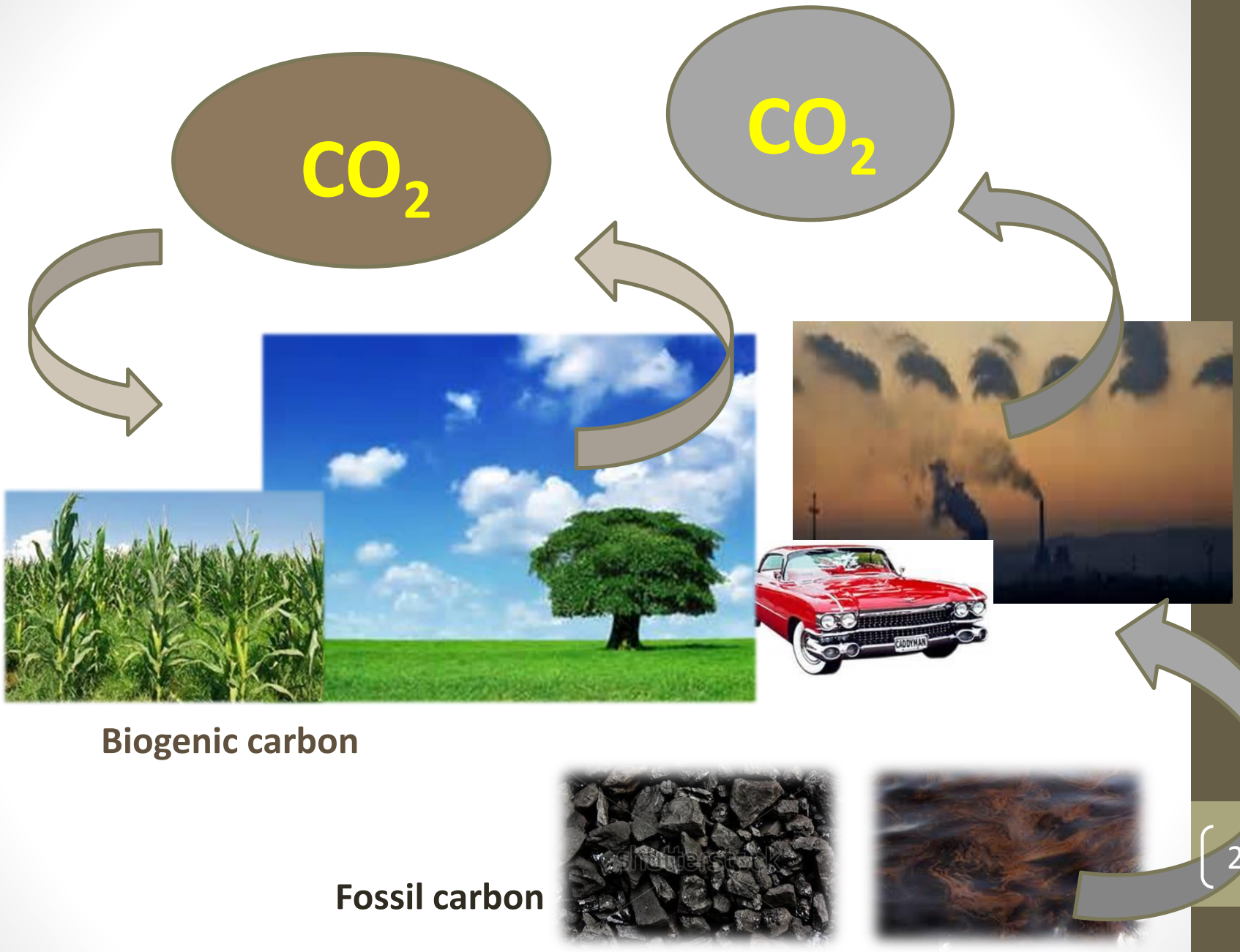
All carbon isotopes take part

^{12}C

^{13}C

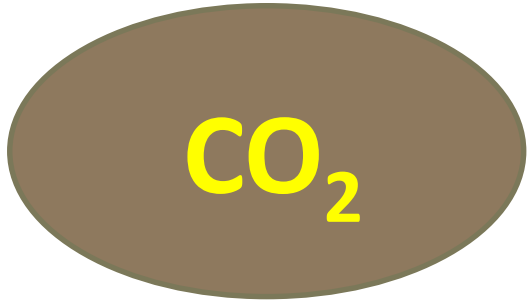
^{14}C

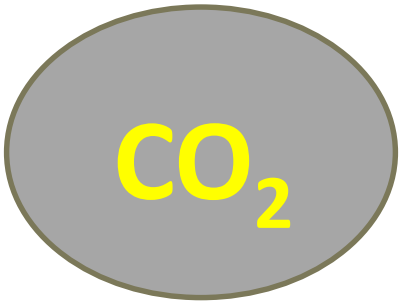
the environmental carbon cycle – carbon is assimilated by terrestrial and aquatic plants in photosynthesis and transfered via the food chain to man.


CO_2
CO_2
Biogenic carbon
Fossil carbon

Carbon isotope fingerprint

Atmosphere
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -8 ‰

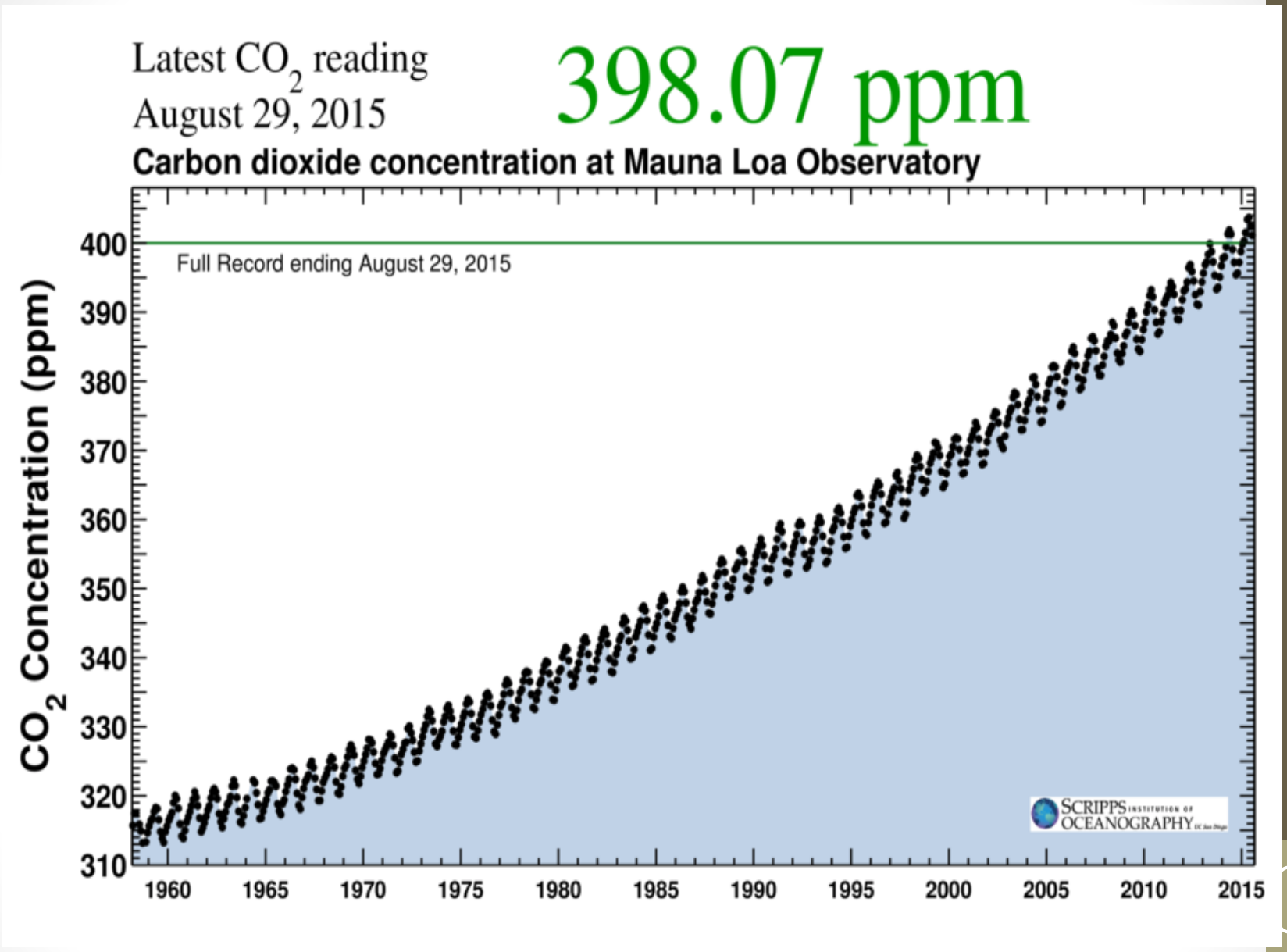




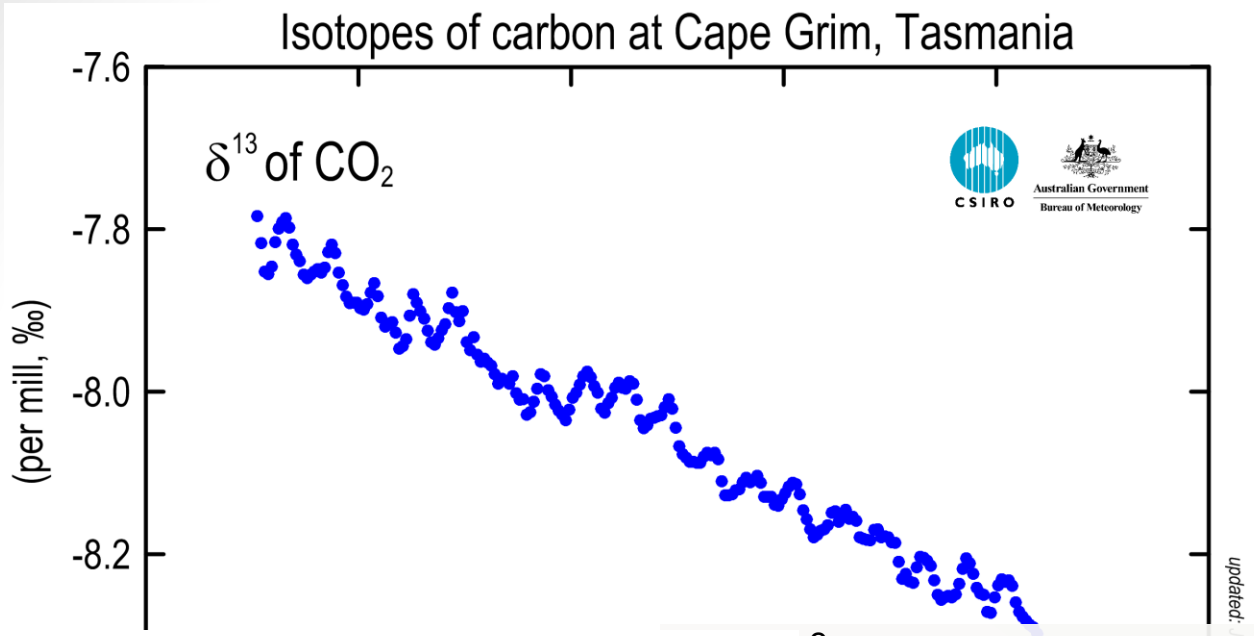
Biogenic carbon

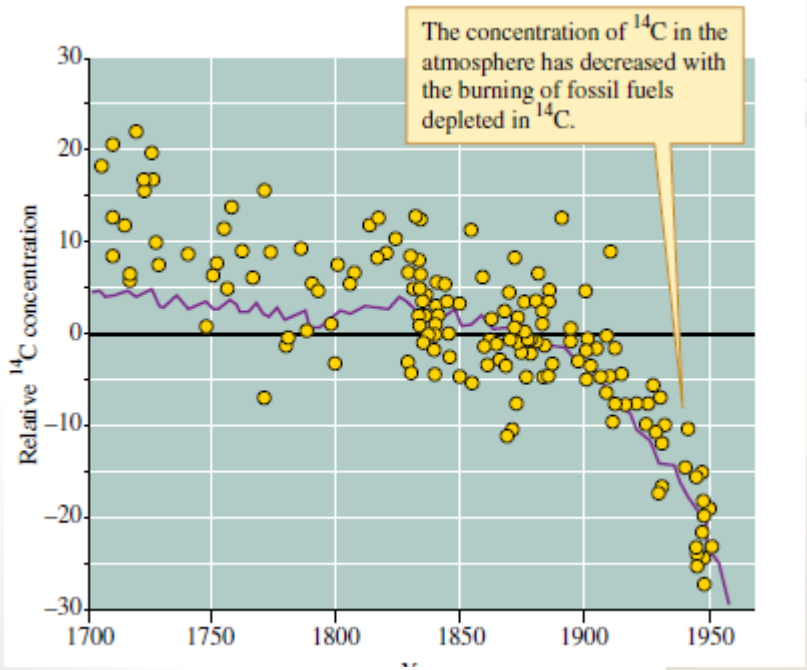
Plants (biosphere)
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -25 ‰ (-12 ‰)

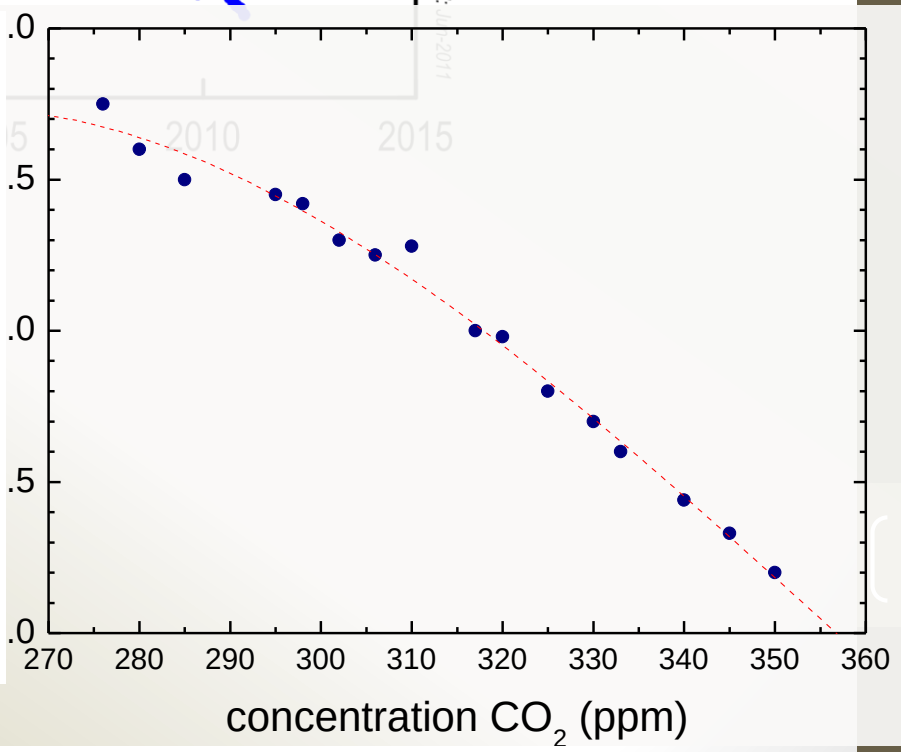
Fossil carbon
$a^{14}C$ = 0 pMC
$\delta^{13}C$ = -25 ‰



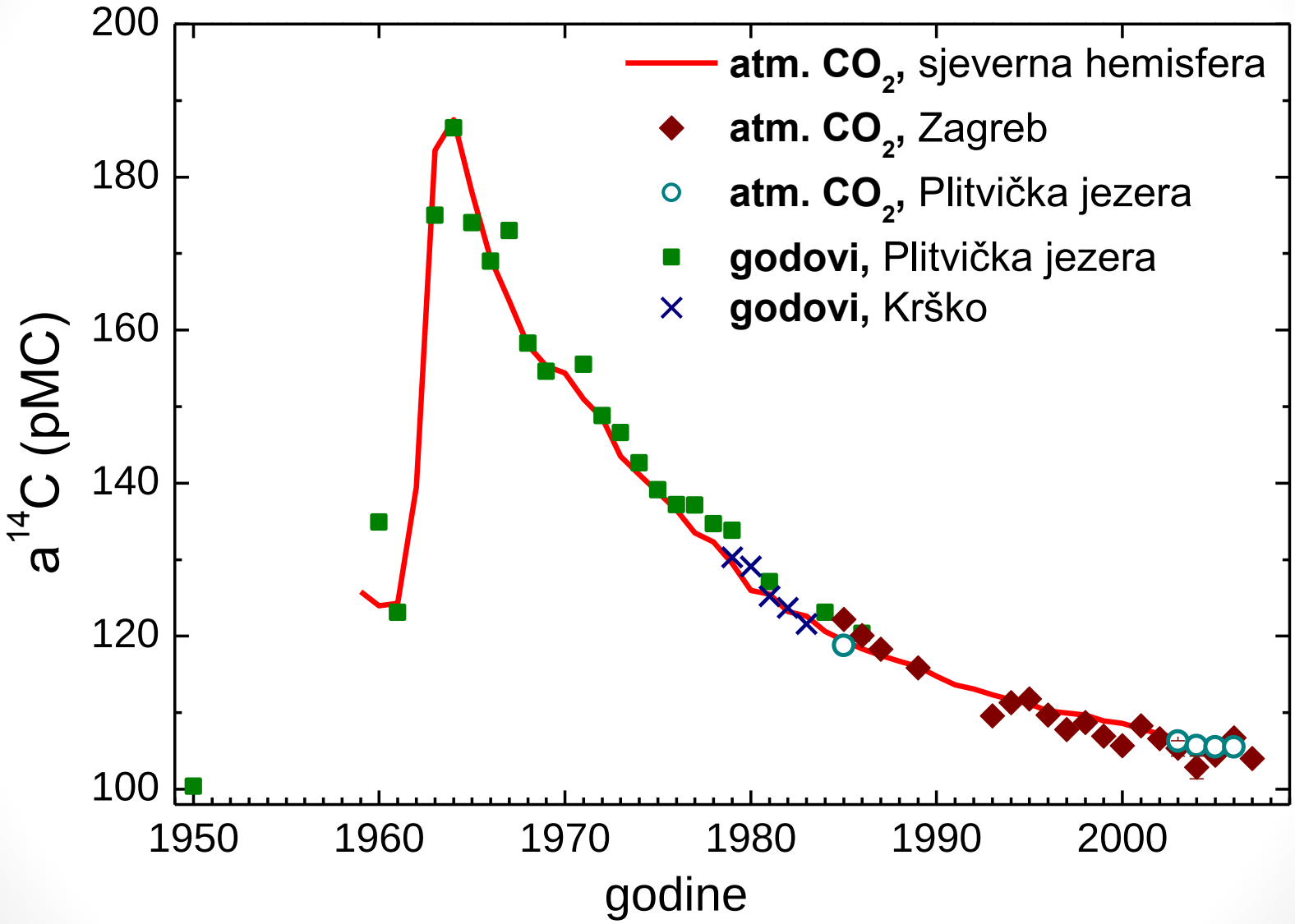
https://scripps.ucsd.edu/programs/keelingcurve/wp-content/plugins/sio-bluemoon/graphs/mlo_full_record.png


Isotopes of carbon at Cape Grim, Tasmania
δ13 of CO2
CSIRO
Australian Government
Bureau of Meteorology
(per mill, ‰)
-7.6
-7.8
-8.0
-8.2
updated:


The concentration of 14C in the atmosphere has decreased with the burning of fossil fuels depleted in 14C.
Relative 14C concentration
30
20
10
0
−10
−20
−30
1700
1750
1800
1850
1900
1950

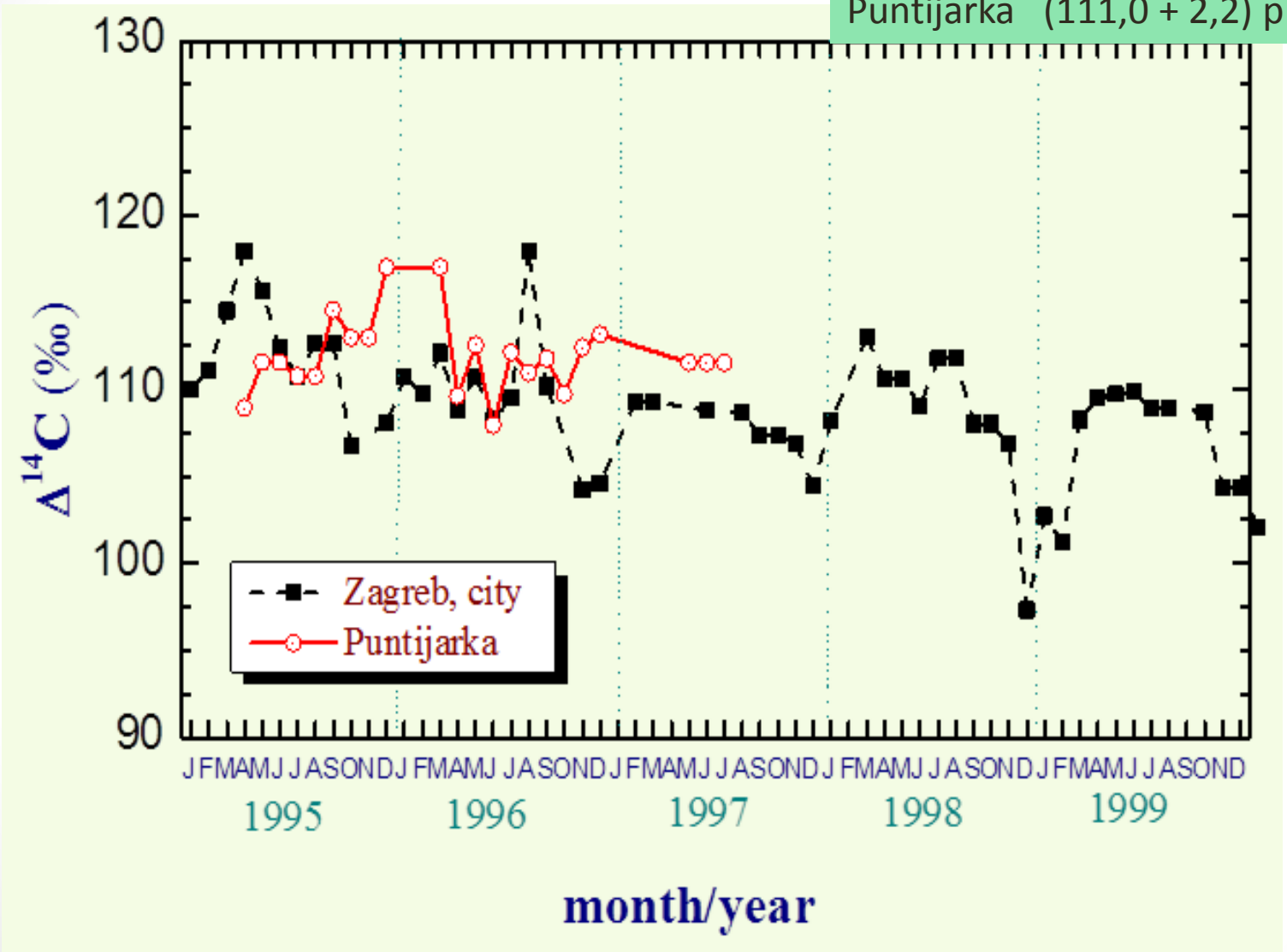

270
280
290
300
310
320
330
340
350
360
concentration CO2 (ppm)

^{14}C aktivnost atmosferskog CO_2 - Hrvatska

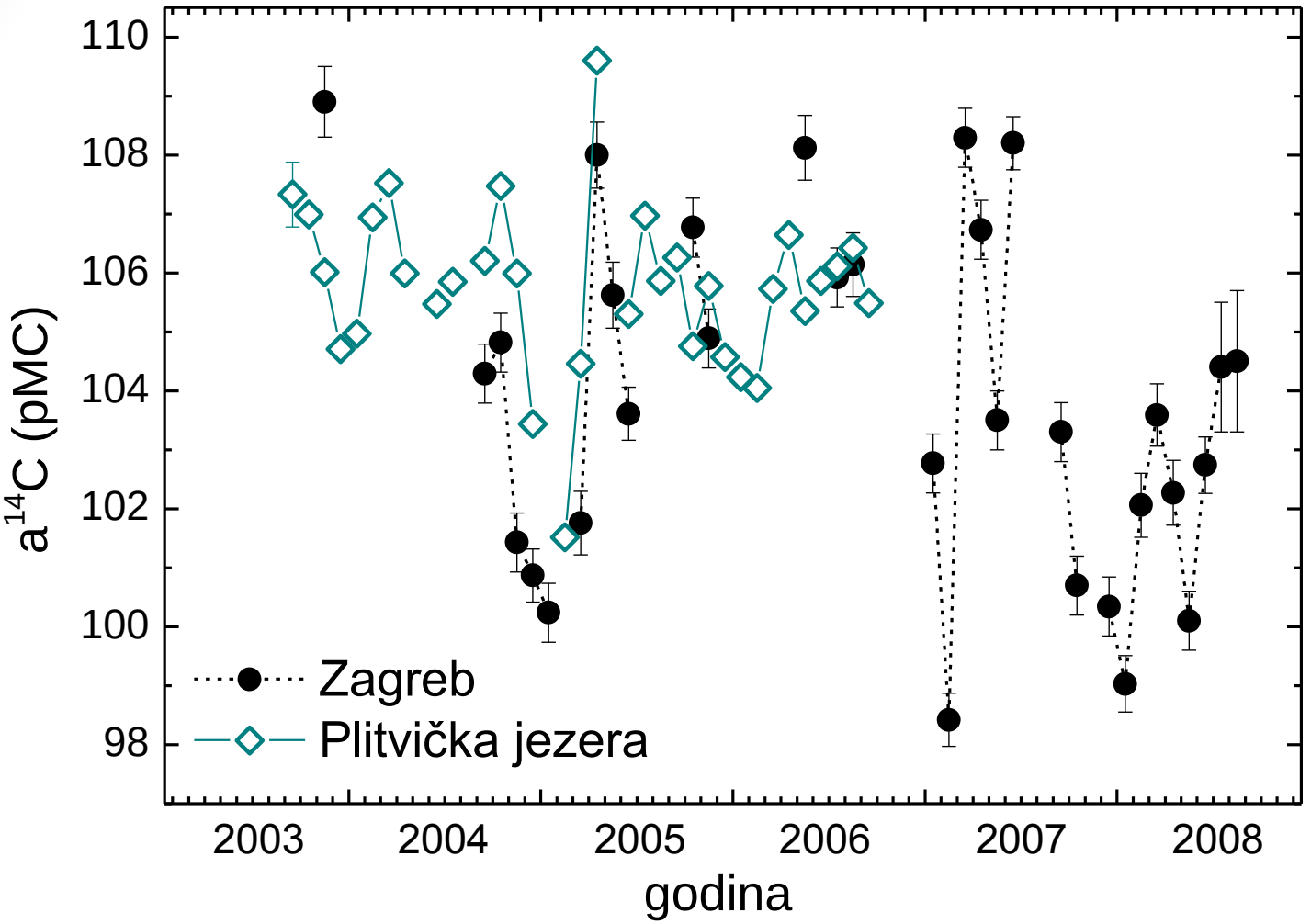


^{14}C u urbanim središtima (1)

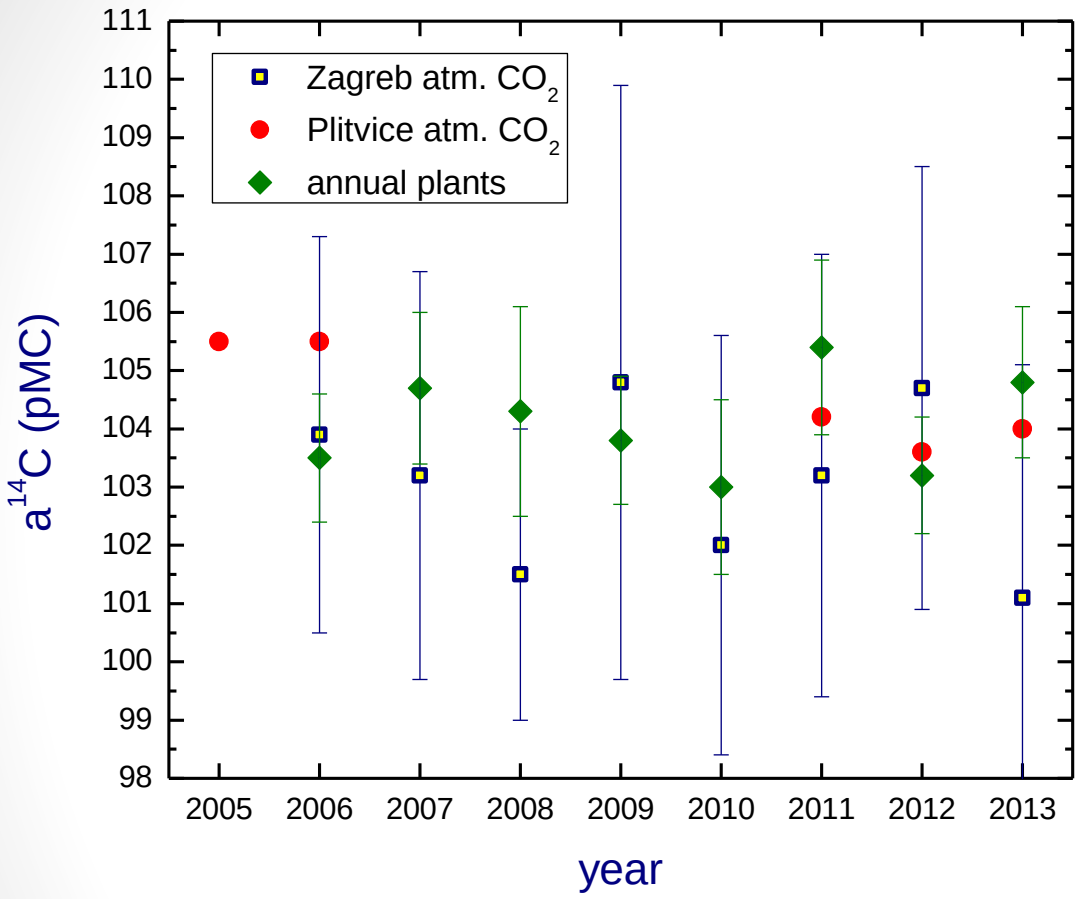
Zagreb (110,0 + 3,4) pMC
Puntijarka (111,0 + 2,2) pMC

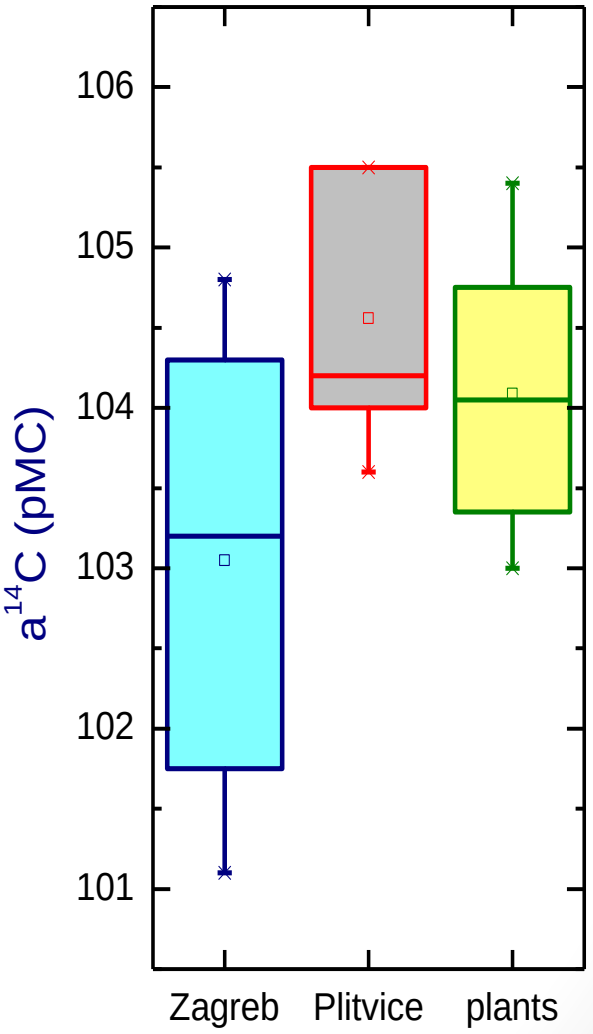


^{14}C u urbanim središtima (2)



Zagreb (104,1 + 2,9) pMC
Plitvička j. (105,7 + 1,5) pMC


Zagreb atm. CO2
Plitvice atm. CO2
annual plants
a14C (pMC)
year
111
110
109
108
107
106
105
104
103
102
101
100
99
98
2005
2006
2007
2008
2009
2010
2011
2012
2013


a14C (pMC)
106
105
104
103
102
101
Zagreb
Plitvice
plants

Toyoizumi (2001, Japan) measured significant difference between plants in mountain and country sites (108 – 110 pMC) and those in the cities, especially near roads with heavy traffic (<100 pMC to 104 pMC)

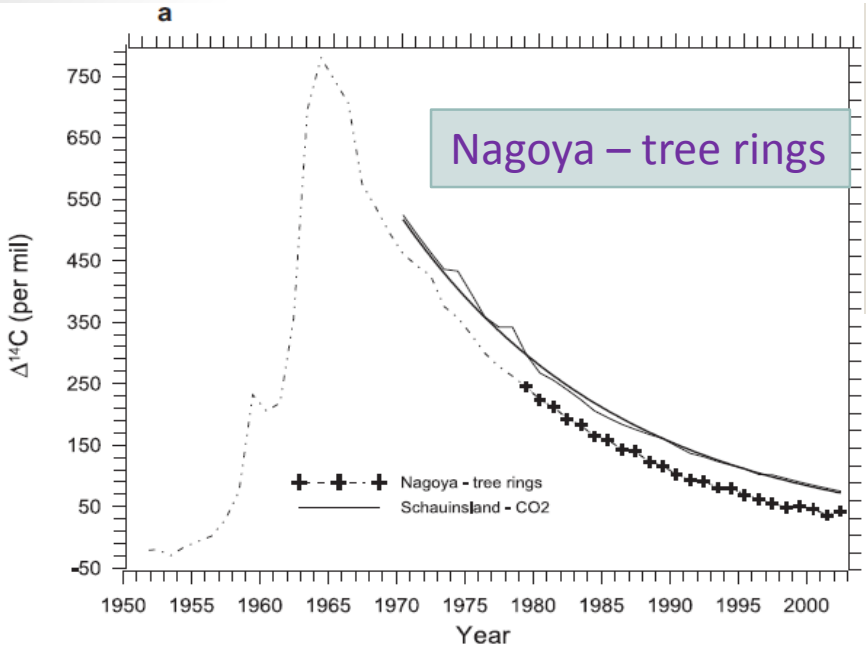
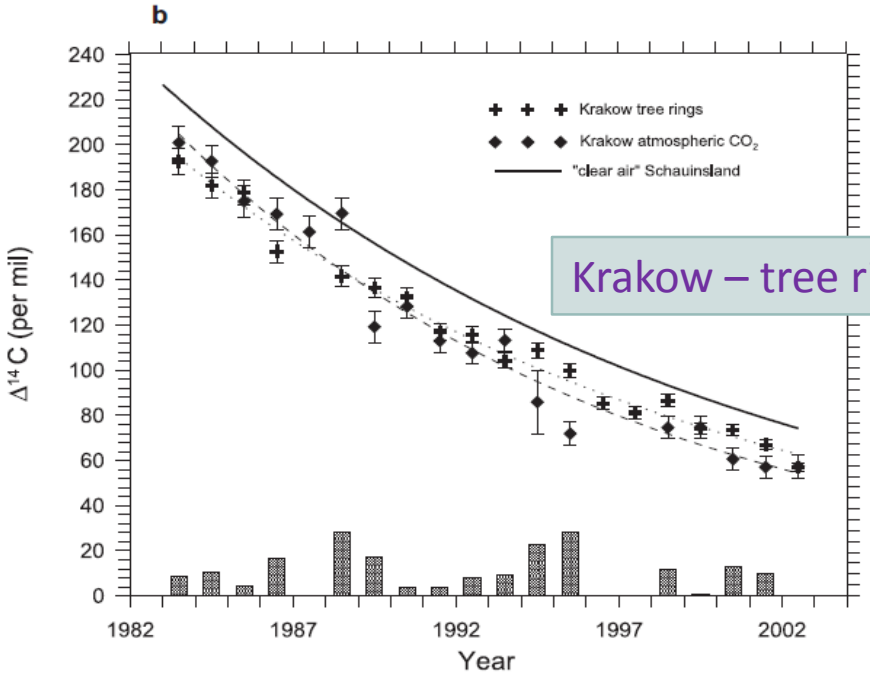


Fig. 2a) Radiocarbon concentration in tree rings from Nagoya, central Japan. The solid line represents annual average values of radiocarbon concentration measured in "clean air" at Schauinsland station (Levin and Kromer, 1997). Dotted line presents radiocarbon concentration in Nagoya for the period 1951-1978 (author's unpublished data).

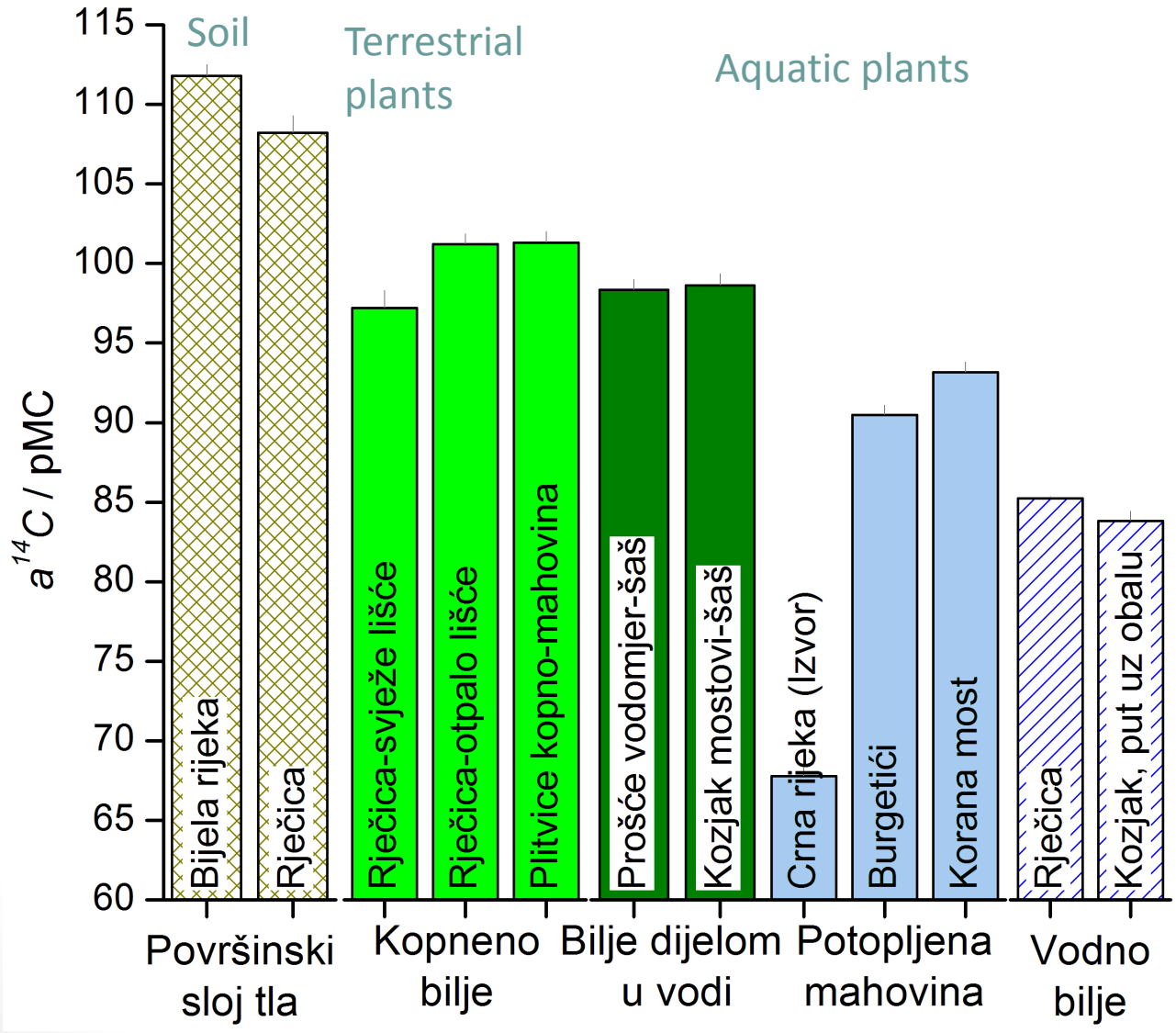


A Rakowski, T Kuc, T Nakamura, A Pazdur: Radiocarbon concentration in urban area, Geochronometria 24 (2005)

Krakow – tree rings and atmospheric CO_2

Fig. 2b) Radiocarbon concentration in tree rings samples and atmospheric CO_2 collected at Kraków, Southern Poland. To the observed data were fitted exponential functions. Solid line presents radiocarbon concentration in "clean air" at Schauinsland station derived from measurement of atmospheric CO_2 (Levin and Kromer, 1997). All atmospheric data represent mean value for the period of April to September corrected by $\delta^{13}C = -25‰$.

^{14}C activity in soil, terrestrial and aquatic plants collected in the Plitvice Lakes area



Veličine i jedinice

Aktivnost	Bq
Koncentracija aktivnosti	
Masena – po kg svježe tvari (FreshWeight – FW)	Bq/kgFW
Masena – po kg suhe tvari (Dry weight – DW)	Bq/kgDW
Volumna – po m^3, po L	Bq/m^3, Bq/L
Specifična aktivnost A_s – po jedinici mase tog elementa!	**Bq/kgC**

Relativna specifična aktivnost ^{14}C

$a^{14}C = A_s$uzorak/A_s standard [pMC = percent Modern Carbon]

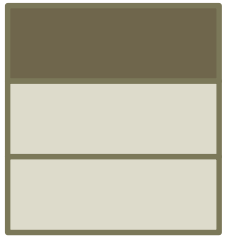
$F^{14}C = A_s$ uzorak/A_s standard [bezdimenzionalna veličina)

A_s standard = 226 Bq/kgC

210 Bq/kgC

1 kgC

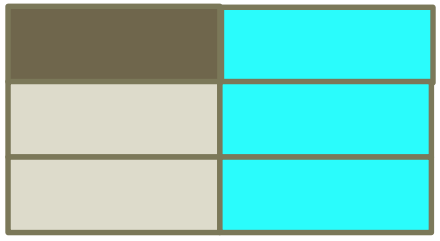
210/3 = 70 Bq/kgDW



1 kgC u 3 kg DW

0.330 kgC/kgDW

70/2 = 35 Bq/kgFW



1 kgC u 6 kgFW

0.17 kgC/kgFW

Neki primjeri udjela ugljika

	Udio ugljika gC / kgFW		Udio C gC/kgDW	Ref.
Lisnato povrće	18 - 65	30	380	IAEA TRS 472 IAEA TECDOC1616
voće	31 - 100	62	410	IAEA TRS 472
žitarice	360 - 430	390	440	IAEA TRS 472
Meso razno	110 - 550	220		IAEA TRS 472
riba	103 - 140 100 - 160	117 120	410	TRS 472 IRSN-14C TECDOC 1616
čovjek		230		

Konverzija specifične aktivnosti ^{14}C u koncentracije aktivnosti

100 pMC = 226 Bq/kgC

Zrak		42 mBq/m^3 zraka
Voda	250 mg/L HCO_3	11,3 Bq/m^3 vode
Voće	60 gC/kgFW	13,56 Bq/kgFW
Riba	120 gC/kgFW	27,2 Bq/kgFW
Uz udio C u DW 400 gC/kgDW		90,4 Bq/kgDW

There are a number of hypotheses concerning the rates of uptake and elimination of radiocesium in fish. The level of radioactive concentration of aquatic biota is commonly defined in terms of a **concentration factor** (R_c) as follows,

$$R_c = \frac{\text{Activity per kg of aquatic biota (wet wt)}}{\text{Activity per liter of water}} \text{ liter/kg.} \qquad (3)$$

bioaccumulation factor = $\frac{\text{nuclide conc in tissue FW [Bq/kgFW]}}{\text{nuclide conc in medium [Bq/L]}}$ [L/kg]

Voda	250 mg/L HCO_3	11,3 Bq/m^3 vode
Riba	120 gC/kgFW	27,2 Bq/kgFW

Ista spec akt ^{14}C!

bioacc f (Fish) = $\frac{\text{27,2 [Bq/kgFW]}}{\text{11,3 E-3 [Bq/L]}}$ = 2407 [L/kg]

bioaccumulation factor for fish

C 50000 (od 5000 do 50000) L/kg fish fresh water

C 2000 (od 2000 do 3000) L/kg fish brakish water

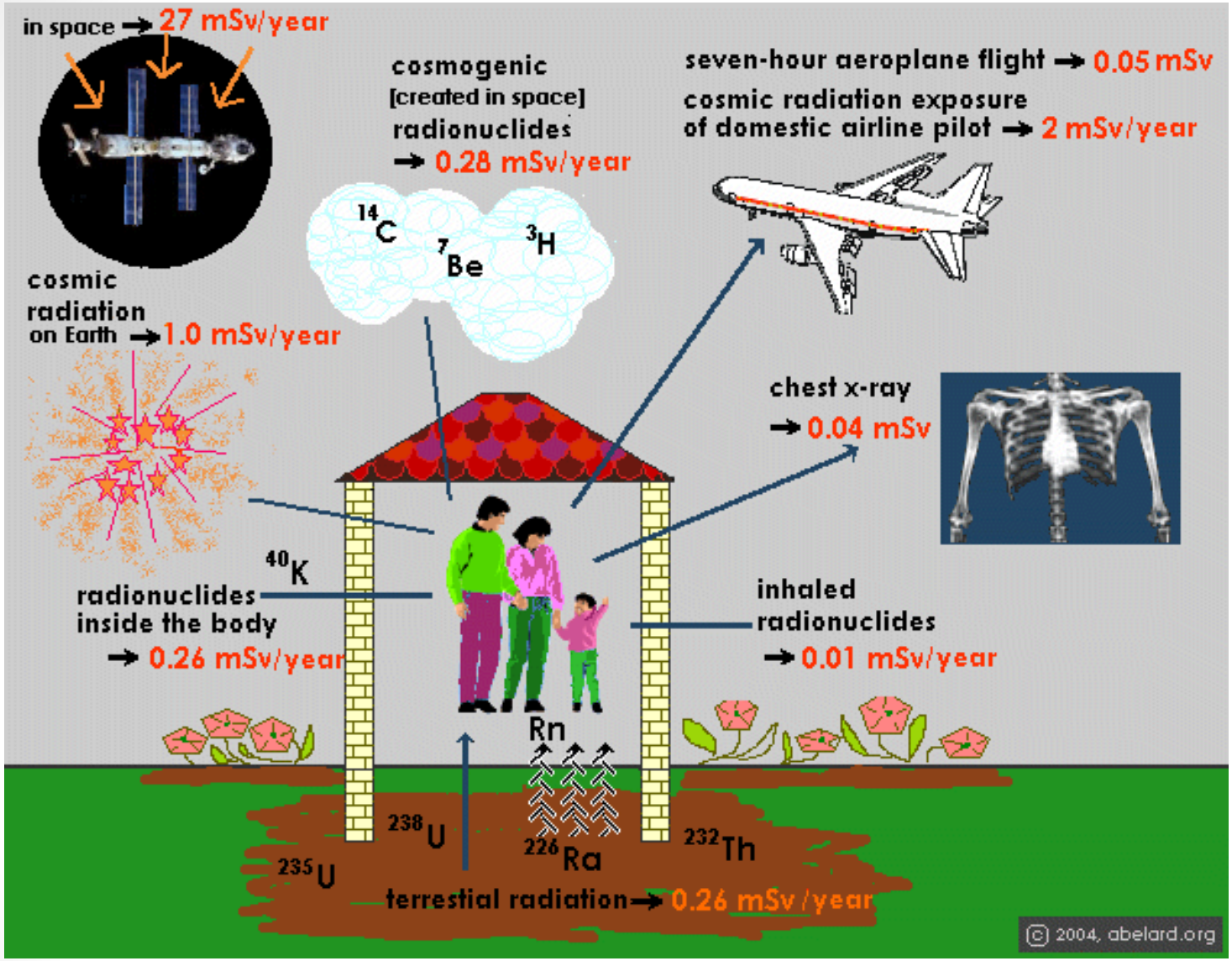
C 4600 (Bq/kgFW)/(Bq/L water) range 1000 - 10000

Baltic Sea 2400 l/kg

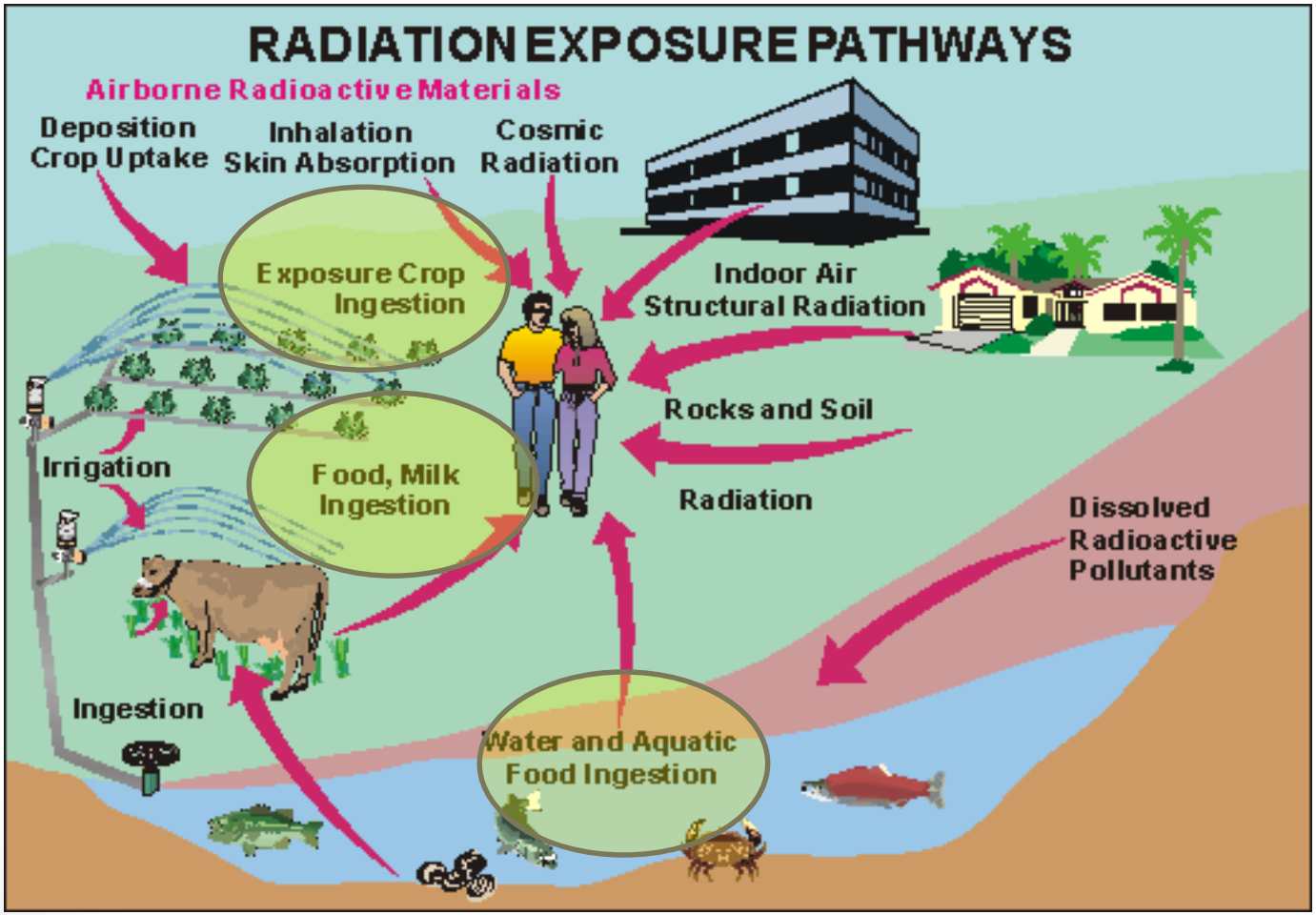
1800 l/kg Swedish west coast

Radiobiološka važnost ^{14}C

- Radiobiološka važnosts ^{14}C: - lako postane dio prehrambenog lanca, prvo preko primarne produkcije (fotosinteze); vrlo je mobilan u okolišu, prelazi iz jednog u drugi "rezervoar"; dugo $T_{1/2}$
- efektivna doza od ^{14}C je samo posljedica ingestije (odnosno. oko <1 % iz drugih izvora, kao inhalacija...) – ^{14}C postaje opasan/rizičan po zdravlje samo ako je unešen u tijelo zbog niske energije emitirane β čestice, ponaša se jednako kao ostali ugljikovi izotopi kako u okolišu tako i u tijelu, brzo se prenosi u organe; of all radionuclides released in routine operation by the nuclear power industry, ^{14}C is likely to produce the largest dose to man
- raspodjela ^{14}C u tijelu je jednolika, i slične doze primaju svi organi i tkiva – critical organ for ^{14}C is the whole body
- Izotopni sastav ^{12}C ^{13}C ^{14}C ovisi o prehrani – »You are what you eat«
- uvijek treba usporediti s dozom na »clean-air« site, tj. na područjima na kojima nema utjecaja ispusta iz NE
- UNSCEAR estimates the radiation dose received by humans (per capita) from the naturally occurring ^{14}C to 15 μSv


in space → 27 mSv/year
cosmogenic
[created in space]
radionuclides
→ 0.28 mSv/year
seven-hour aeroplane flight → 0.05 mSv
cosmic radiation exposure
of domestic airline pilot → 2 mSv/year
^{14}C
^{7}Be
^{3}H
cosmic
radiation
on Earth → 1.0 mSv/year
chest x-ray
→ 0.04 mSv
^{40}K
radionuclides
inside the body
→ 0.26 mSv/year
inhaled
radionuclides
→ 0.01 mSv/year
Rn
^{238}U
^{226}Ra
^{232}Th
^{235}U
terrestial radiation → 0.26 mSv /year
© 2004, abelard.org

assessment model of the dose should be "fit for purpose", ie., it should not exclude, or poorly represent, any process that is known or suspected of having an important influence on radionuclide behaviour, and equally, it should not attempt to include detail that is not relevant to either the spatial or temporal scale of the assessment



Physiologically, only CO_2 form of carbon is of interest: nearly all of carbon content in man comes from the atmosphere via plant and animal products ingested by man (inhalation pathway contributes <1% to the total dose)

	unit	ingestion	inhalation
Daily carbon intake	g C	300	3
Dose conversion factor e	Sv/Bq	$5{,}8 \times 10^{-10}$	$6{,}36 \times 10^{-12}$
Effective dose	**Sv/yr**	**14,4 E-6**	**1,6 E-9**

$$E = e \times a^{14}C \times m \times t$$

to asses the radiation dose rate (by consumption/ingestion):

- activity conc in foodstaffs, $a^{14}C$ **[Bq/kgC]**
- relevant consumption rates - Dnevni unos ugljika hranom: 0,3 kg, ICRP, 1996
- ICRP ingestion dose coefficients are needed - $5{,}8 \times 10^{-10}$ Sv/Bq

$$E = e \times a^{14}C \times m \times t$$

however, obtaining the consumption data for particular areas may not be simple;

luckily – the specific ^{14}C activity in all types of (terrestrial) foodstaff is the same

IAEA TRS472, TECDOC 1616 (2009)

The assumption of full specific activity equilibrium in terrestrial environment is completely satisfactory for ^{14}C releases to the atmosphere, if, as it is usual, the ^{14}C is emitted as CO_2. This is the only form that is readily taken up by plants, so that active carbon is incorporated into the plant dry matter via photosynthesis at the same rate as stable carbon. Therefore, the ^{14}C conc in Bq/gC is the same in the plants as it is in the air (terrestrial environment)

$$a^{14}C_{air} = a^{14}C_{plants} = a^{14}C_{animals} = a^{14}C_{man}$$ [Bq/kgC] specific activity ^{14}C

$C_{air} / S_{air} = C_{pFW} / S_{pFW}$ **[Bq/m³]/[gC/m³]=** **[Bq/kgFW]/[kgC/kgFW]** ➔ **[Bq/kgC] = [Bq/kgC]**	C_{pFW} – ^{14}C conc in **plant** [Bq/kg fresh weight] S_{pFW} – fraction of carbon per kg plant FW (kgC/kgFW) C_{air} – ^{14}C conc in air [Bq/m³] S_{air} – fraction of carbon in air [kgC/m³]
	S_{air} 0.20 g/m³ = 2 10^{-4} kgC/m³ S_{pFW} varies 30 – 410 g/kgFW S_{pDW} 310 – 470 gC/kgDW
animal products $C_{aFW} / S_{aFW} = f \times C_{pFW} / S_{pFW}$	f fraction of »contaminated« animal feed egg Segg 160 gC/kgFW meat Smeat 200 – 550 gC/kgFW

Aquatic environment

several carbon pools existing: DIC, DOC (in water column), PIC, POC (mostly in sediments) different aquatic organisms are exposed to different carbon pools

DIC is the dominant carbon pool accessed by most aquatic organisms, taken up by most aquatic plants and animals that are important for human consumption

Moreover, DIC is the form of carbon normally released by NP to aquatic systems, the most common form in the water column, and the most easily measurable form of carbon → thus, it is reasonable to use DIC as the basis for spec.activity (SA) model for fish

$$\alpha^{14}C_{fish} = C_{fishFW} / S_{fishFW} = \alpha^{14}C_{DIC}$$

[Bq/kgC] = [Bq/kgfishFW]/[gC/kgfishFW] = [Bq/kgC]

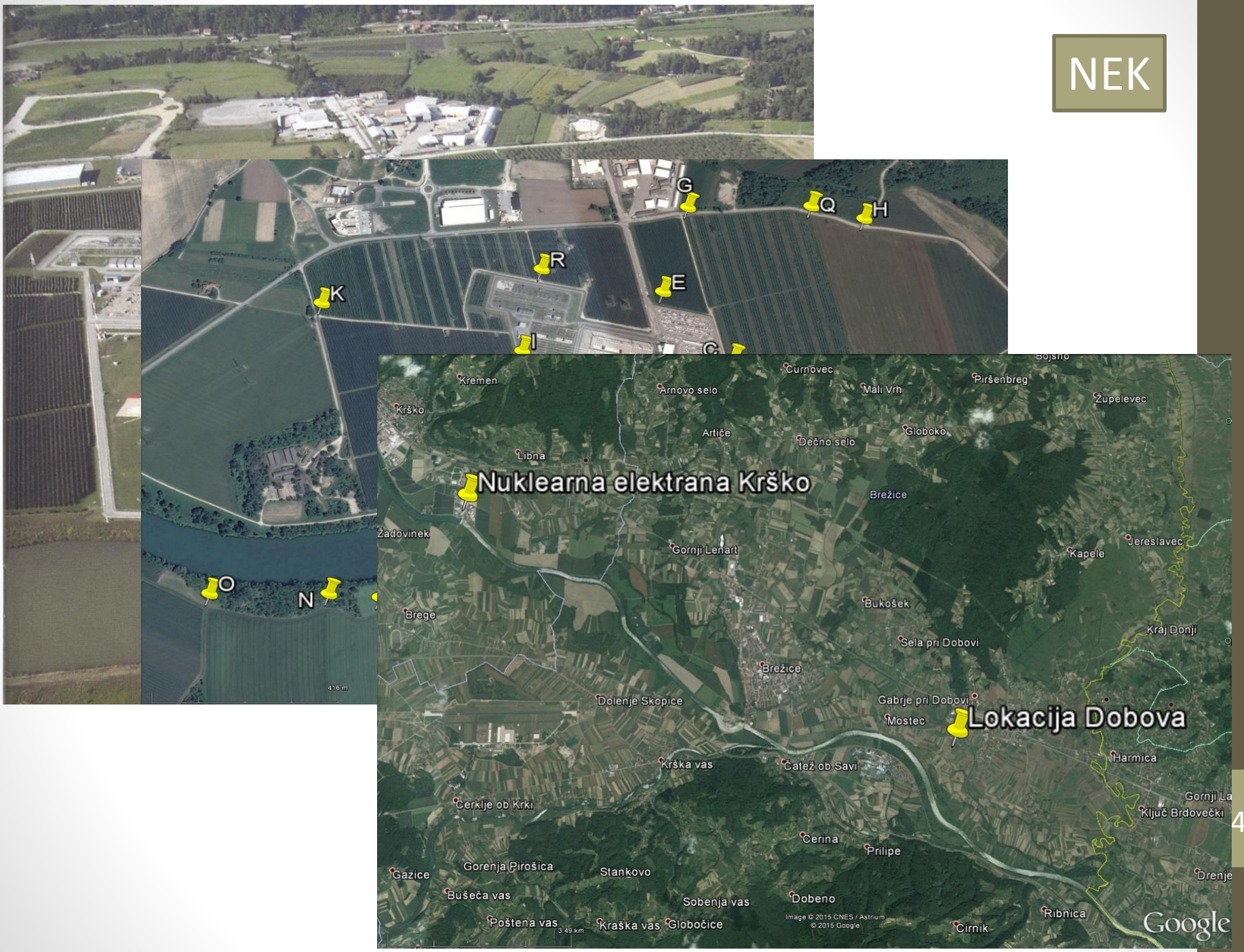
S_{fishFW} = 120 gC/kgFW

Monitoring

- općenito – komponente programa monitoringa su: lokacije (outside plant perimeter), environmental media and isotopes/nuclides of interest; monitoring frequency; analytical frequency, assessment of data
- monitoring oko NE obično uključuje: atmosferski CO_2, biota – s godišnjim periodom rasta, odnosno »integrated samplers covering the vegetation period«;
- tree rings integrate ^{14}C concentrations during spring-summer-autumn growing season, not during winter; tree rings are not sensitive to short-term increases caused by single releases of ^{14}C from NPP, but they integrate impacts from both nuclear and fossil CO_2 sources on the local environment, and thus can indicate long-term trends in ^{14}C biospheric concentrations
- atmosferski CO_2 uzorkuje se u tjednim, dvotjednim, mjesečnim ili dvomjesečnim intervalima; ne može se direktno usporediti s biljkama koje integriraju 14C za vrijeme vegetacijskog razdoblja; budući da ni emisije ni meteorološki uvjeeti nisu konstantni u vremenu, može doći do razlike u srednjim vrijednostima u kraćim i dužim vremenskim razdobljima
- uvijek treba usporediti područje u kojem se očekuje utjecaj NU s područjem bez tog utjecaja (dovoljno udaljeno, bez dodatnih izvora »kontaminacije« - npr. gradovi, industrija)

- oko NEK je od 2006. uspostavljena mreža mjesta uzorkovanja: 2 lokacije za CO_2 unutar NEK, lokacije uz ogradu NEK (unutarnji krug) i vanjski krug, kontrolna točka Dobova 12 km
- uzorkuje se jednogodišnje bilje/plodovi uvijek na istim lokacijama, dva puta godišnje
- usporedba raznih vrsta bilja na istoj lokaciji
- mjerenja $\delta^{13}C$ u raznim vrstama bilja, te nakon karbonizacije
- Od 2013. u tekućim efluentima
- Jednom ribe

NEK


G
Q
H
R
K
E
I
O
N
Nuklearna elektrana Krško
Lokacija Dobova
Kremen
Krško
Arnovo selo
Curnovec
Mali Vrh
Piršenbreg
Župelevec
Artiče
Globoko
Dečno selo
Libna
Brežice
Žadovinek
Gornji Lenart
Jereslavec
Kapele
Bukošek
Brege
Kraj Donji
Sela pri Dobovi
Brežice
Dolenje Skopice
Gabrje pri Dobovi
Mostec
Harmica
Krška vas
Čatež ob Savi
Cerklje ob Krki
Ključ Brdovečki
Cerina
Prilipe
Gazice
Gorenja Pirošica
Stankovo
Bušeča vas
Sobenja vas
Dobeno
Poštena vas
Kraška vas
Globočice
Ribnica
Cirnik
Image © 2015 CNES / Astrium
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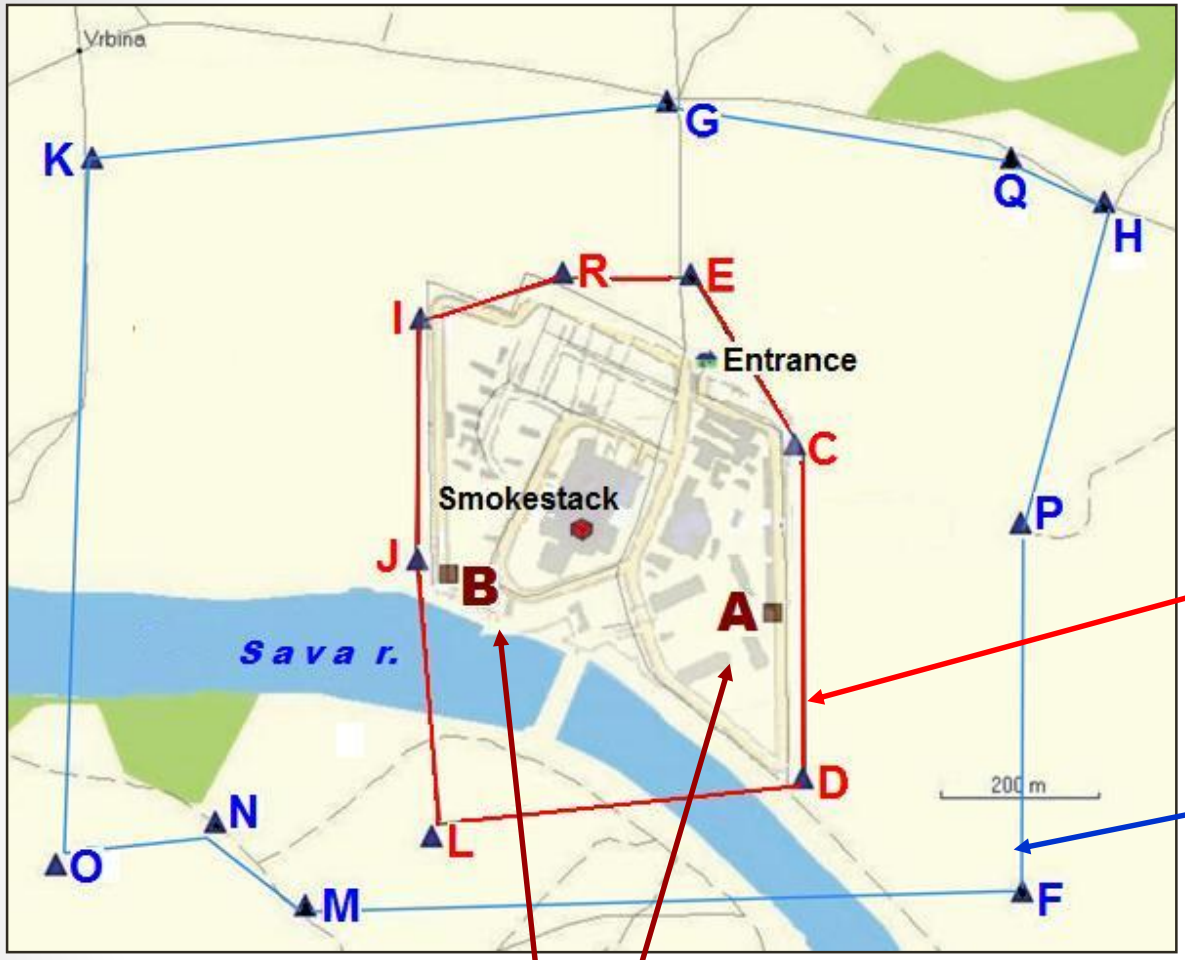
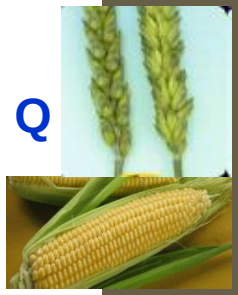
Točke uzorkovanja (2006-2015)



Biološki uzorci
(VI/VII, IX/X)

Unutarnji krug (≤300 m)
C, **D**, **E**, **I**, **J**, **L**, **R**

Vanjski jrug (~1 km):
F, **G**, **H**, **K**, **M**, **N**, **O**, **P**, **Q**



Atmosferski CO_2
(svaka 2 mjeseca)

Kontrolna točka Dobova
(12 km od NEK)

C

J

I

L

M

Atmospheric CO_2

Tray with saturated NaOH (location **B**)

- **Absorption of atmospheric CO_2 on saturated NaOH during 2-month periods forming Na_2CO_3** (shorter period exceptionally during the refuelling process)**;**
- **Na_2CO_3 reacts with HCl and obtained CO_2 is transformed to benzene;**
- **Measurement of ^{14}C activity in liquid scintillation counter (LSC) *Quantulus 1220.***


Z-4349
Z-4342

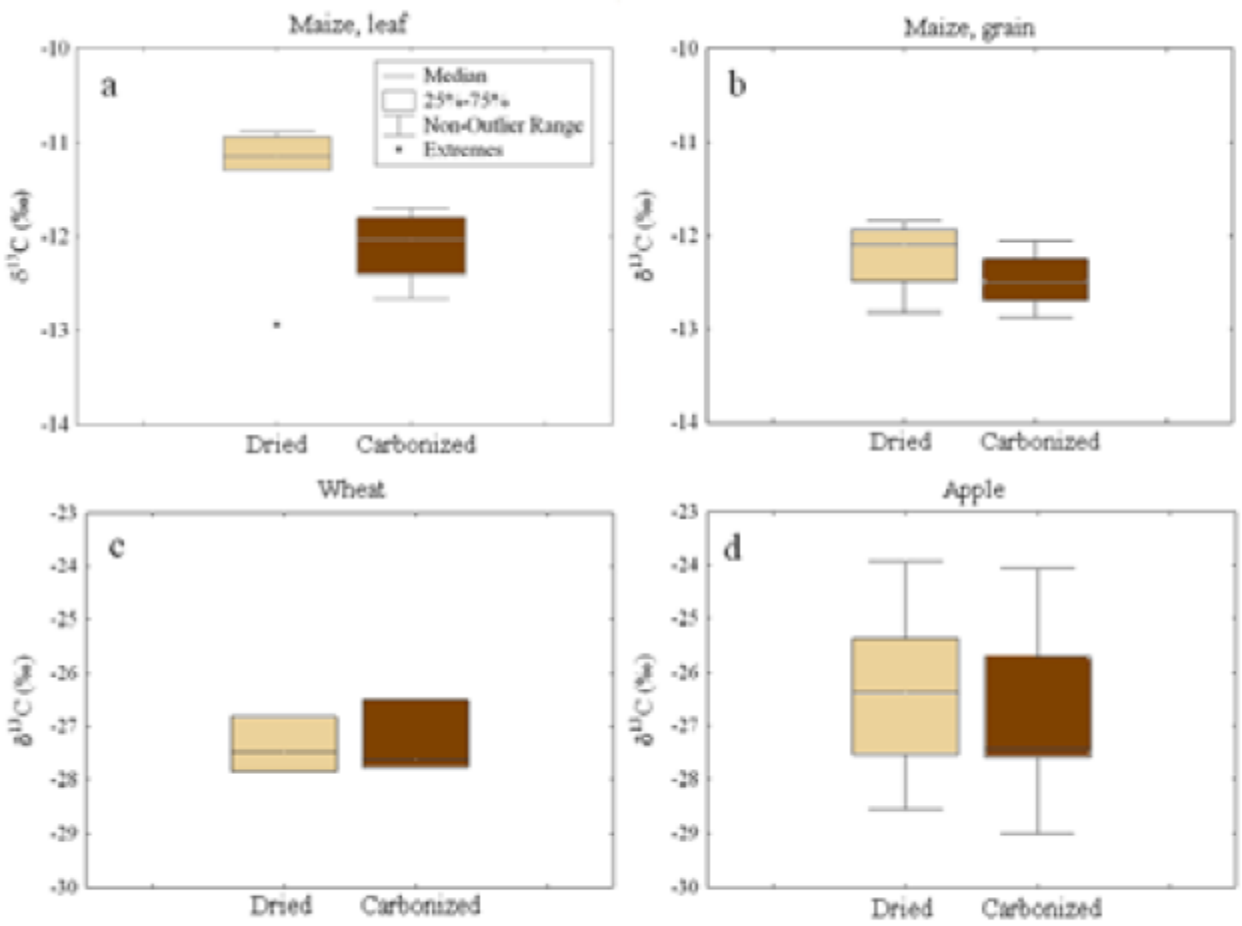
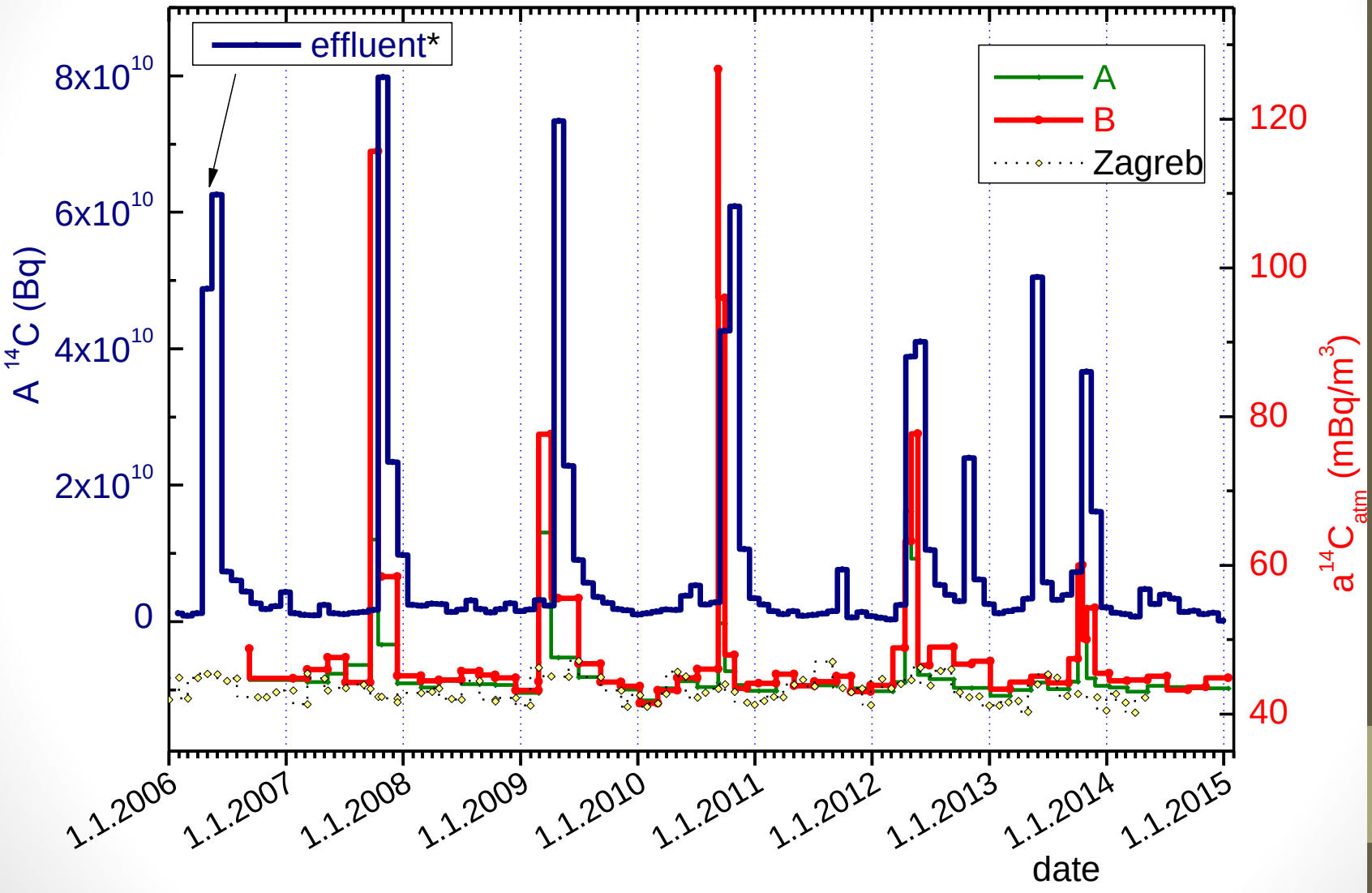


Figure 5: $\delta^{13}C$ of dried and carbonized maize leaf (a), maize grain (b), wheat (c) and apple (d) samples.

Atmosferski CO_2

Usporedba aktivnosti ^{14}C na lokacijama A i B s onom u Zagrebu, te s ukupno ispuštenom aktivnošću A u zračnim ispustima



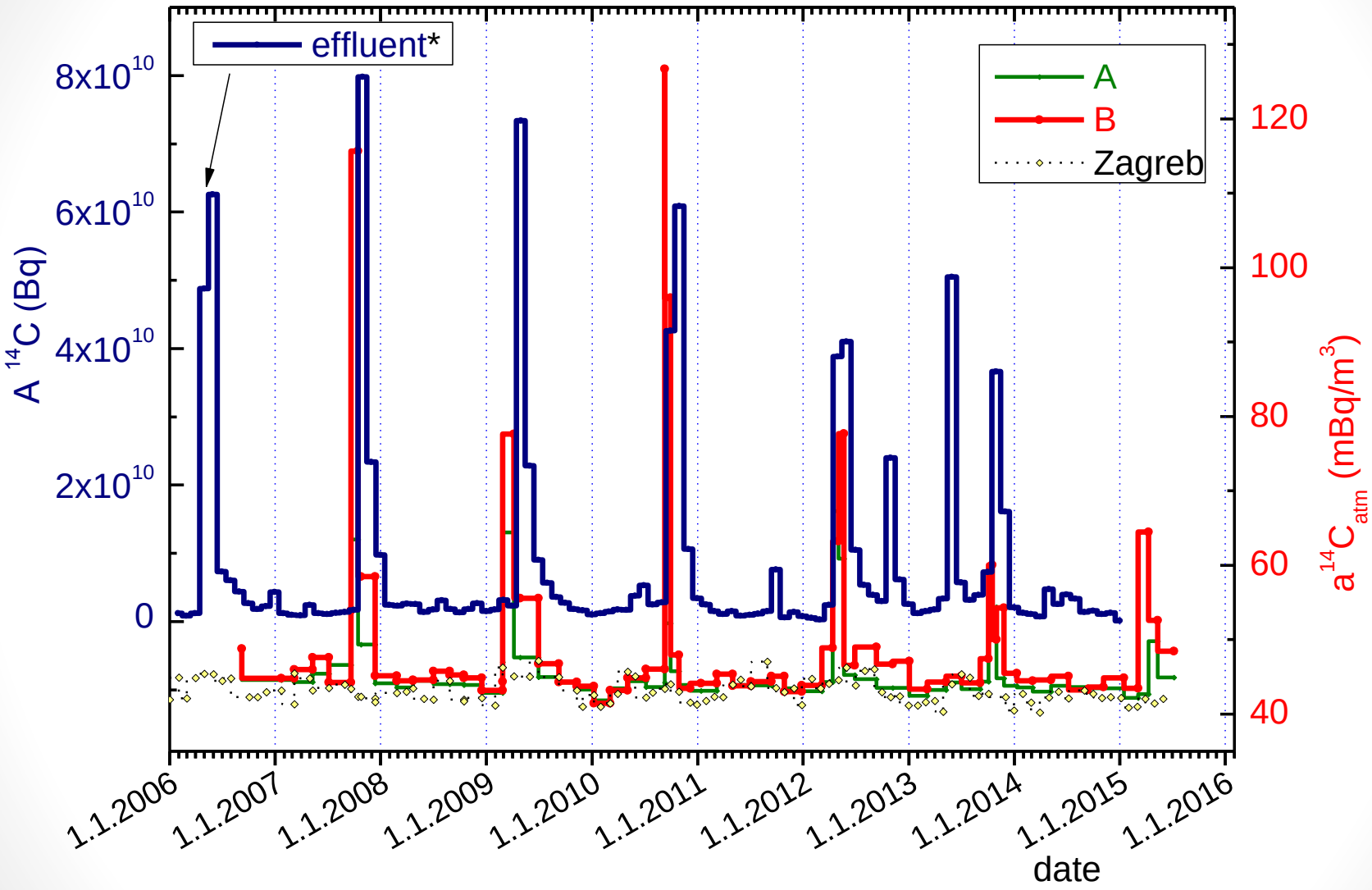
* measured at J. Stefan Inst., Ljubljana, Slovenia

Prosječne i maksimalne vrijednosti $a^{14}C_{atm}$ [pMC] na lokacijama NEK-A i NEK-B i u Zagrebu u razdoblju 2006.–2014.

Osjenčane su godine u kojima je proveden remont.

godina	**NEK-A**		**NEK-B**		**Zagreb**	
	srednja vr.	maks.	srednja vr.	maks.	srednja vr.	maks.
2006	nedovoljno podataka	106,6	nedovoljno podataka	116,1	103,9 ± 3,4	108,1
2007	112,2 ± 12,4	151,1	127,6 ± 46,0	275,4	103,2 ± 3,5	108,3
2008	104,5 ± 1,1	105,9	106,8 ± 1,1	109,0	101,5 ± 2,5	105,9
2009	110,6 ± 14,1	153,3	116,9 ± 23,9	184,9	104,8 ± 5,1	112,2
2010	105,7 ± 6,4	124,3	132,0 ± 64,3	301,7	102,0 ± 3,6	108,8
2011	104,9 ± 2,1	108,2	105,4 ± 1,9	108,1	103,2 ± 3,8	112,1
2012	116,8 ± 22,5	160,1	125,9 ± 27,7	185,0	104,7 ± 3,8	110,2
2013	109,1 ± 10,0	129,5	114,8 ± 13,4	143,0	101,1 ± 4,0	108,1
2014	103,6 ± 0,7 N=5	104,3	105,5 ± 1,7 N=6	107,4	*99,2 ± 2,3 N=4*	*101,8*

2015. remont

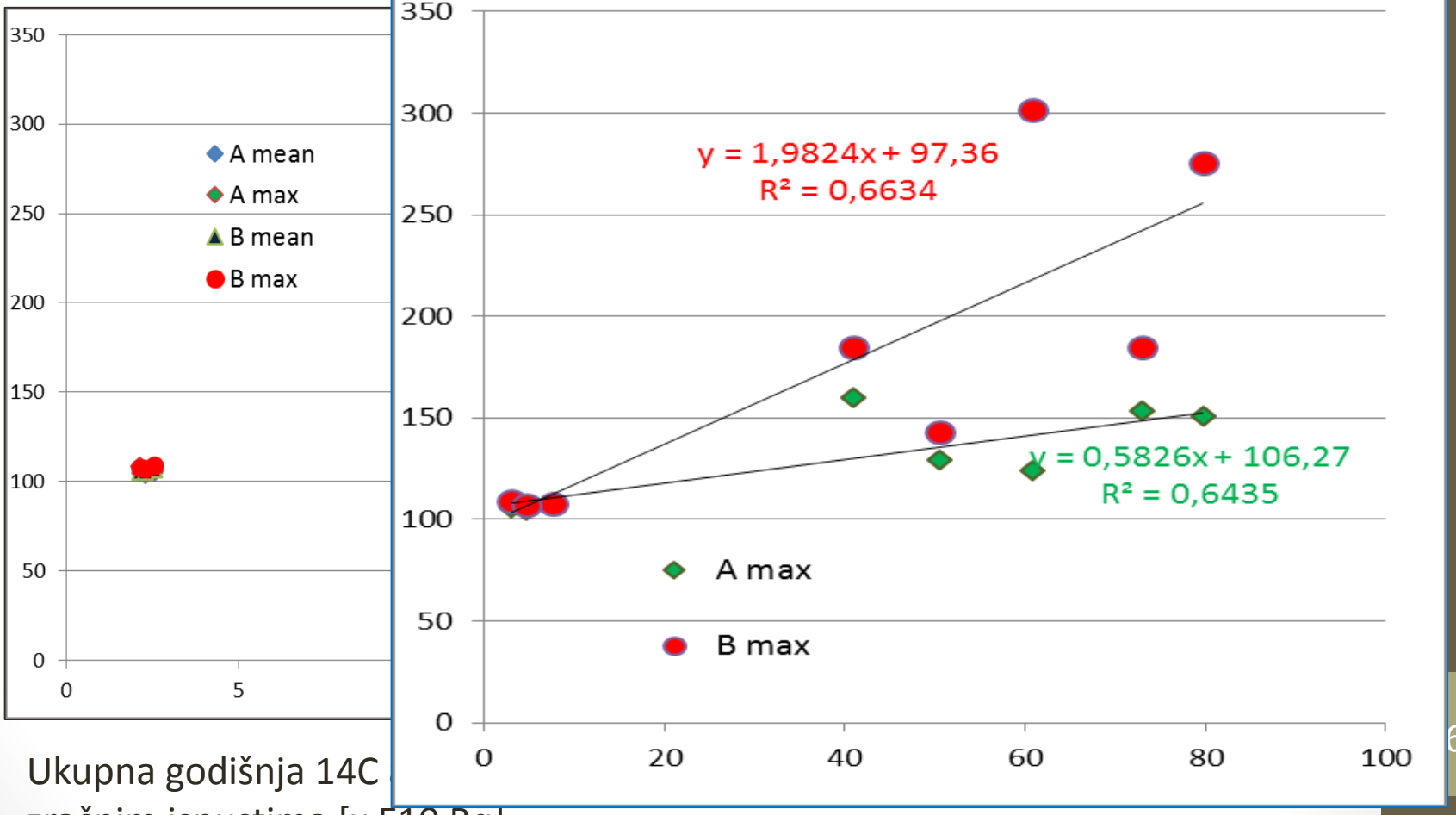


* measured at J. Stefan Inst., Ljubljana, Slovenia

Atmosferski CO_2

Usporedba ispuštene ^{14}C aktivnosti i izmjerene atmosferske ^{14}C aktivnosti na lokacijama A i B

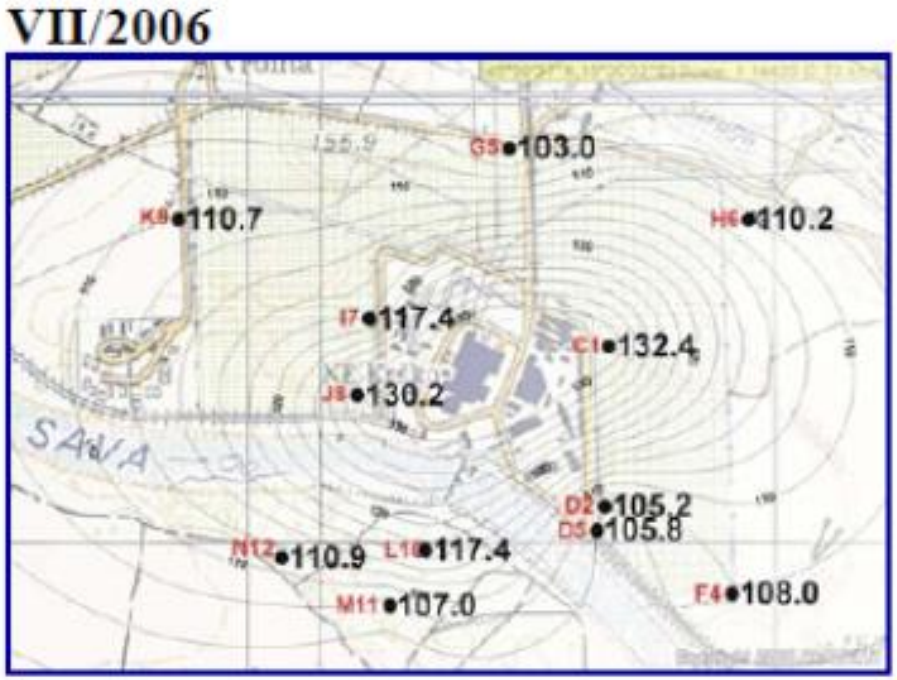
^{14}C aktivnost u atmosferi [pMC]

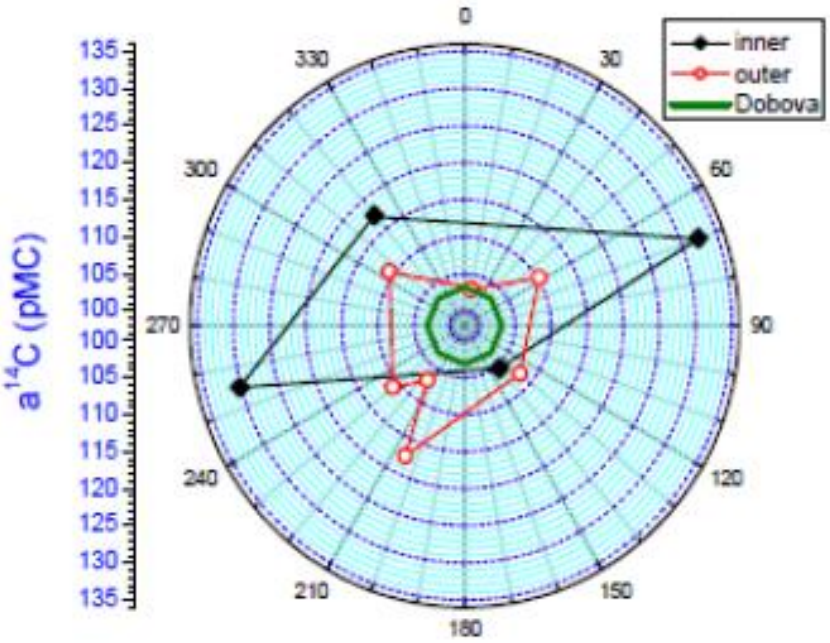


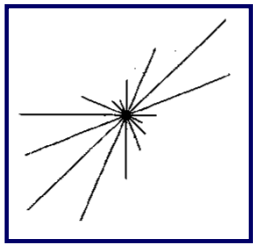
Ukupna godišnja 14C
zračnim ispustima [x E10 Bq]

Najviša mjesečna ^{14}C aktivnost u zračnim ispustima [x E9 Bq]

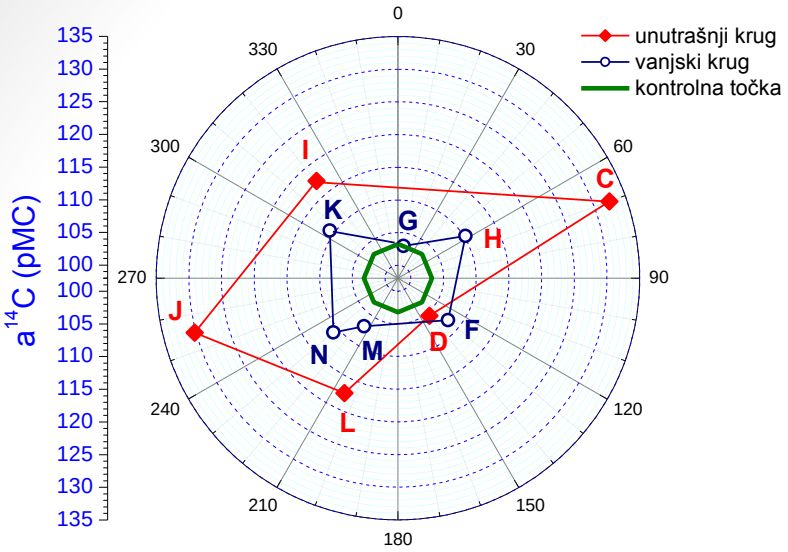
^{14}C u biološkim uzorcima, NEK prostorna raspodjela

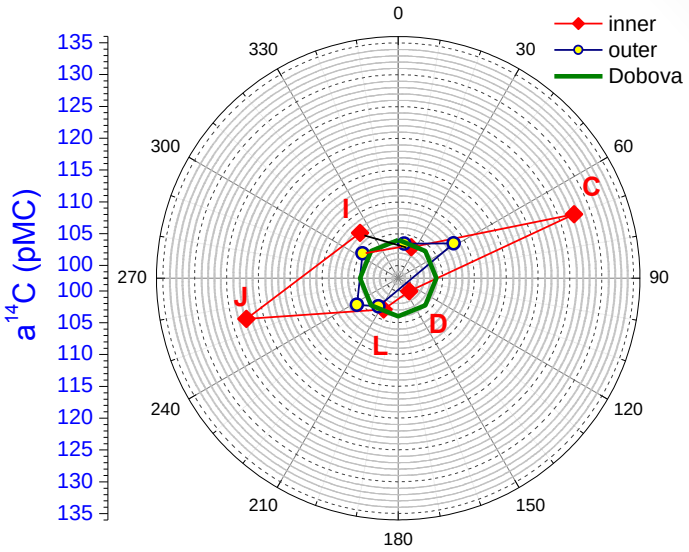


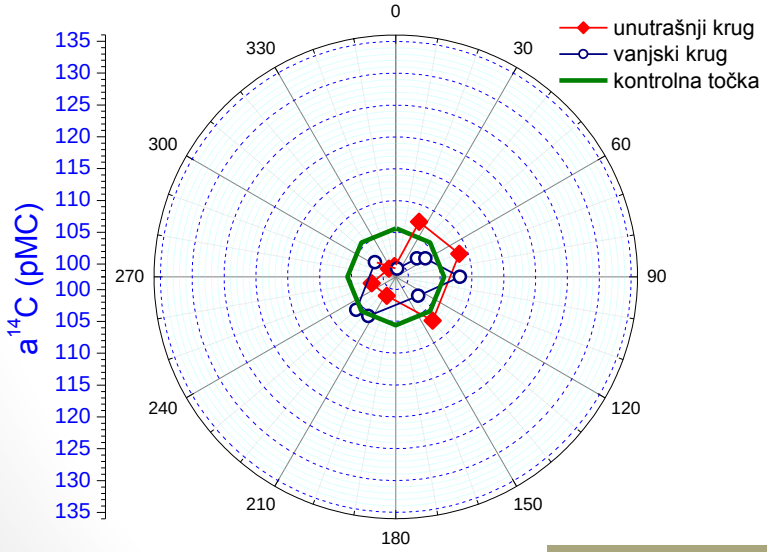


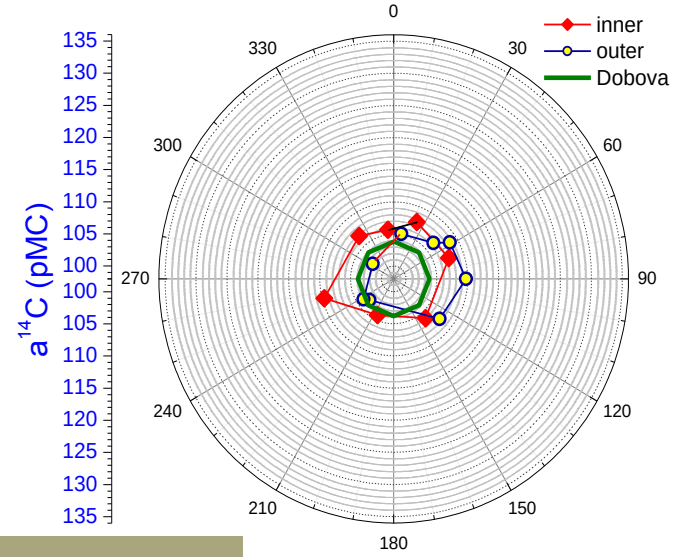


7/2006 remont 10/2006



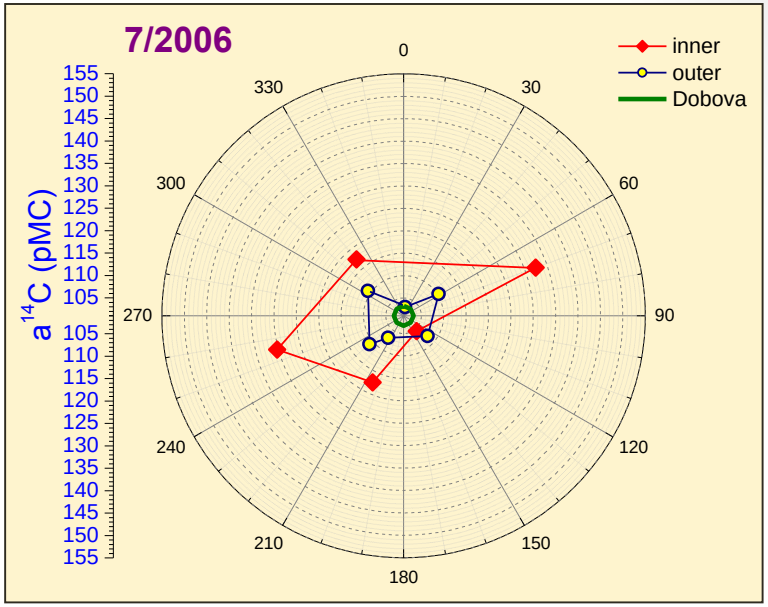


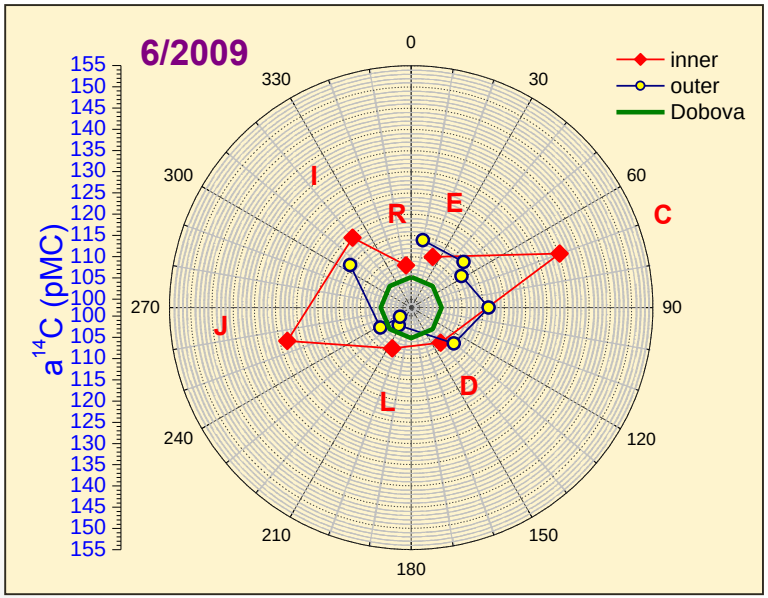


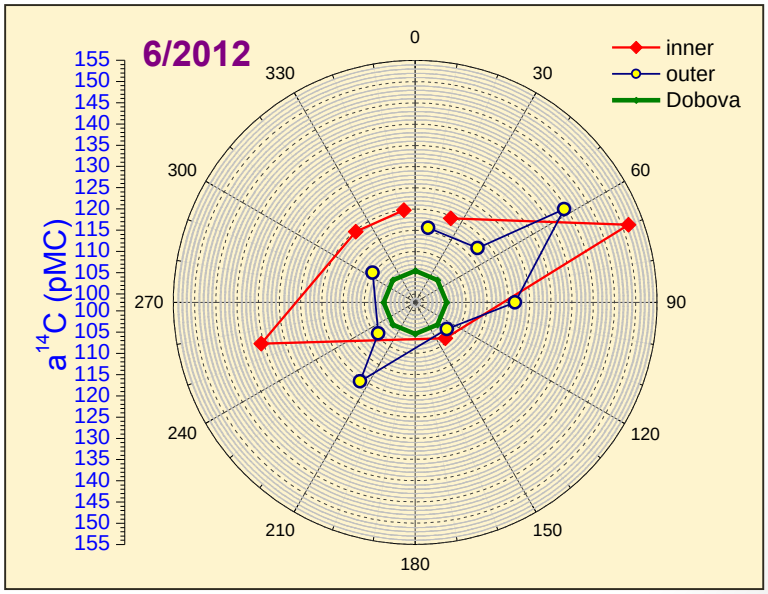


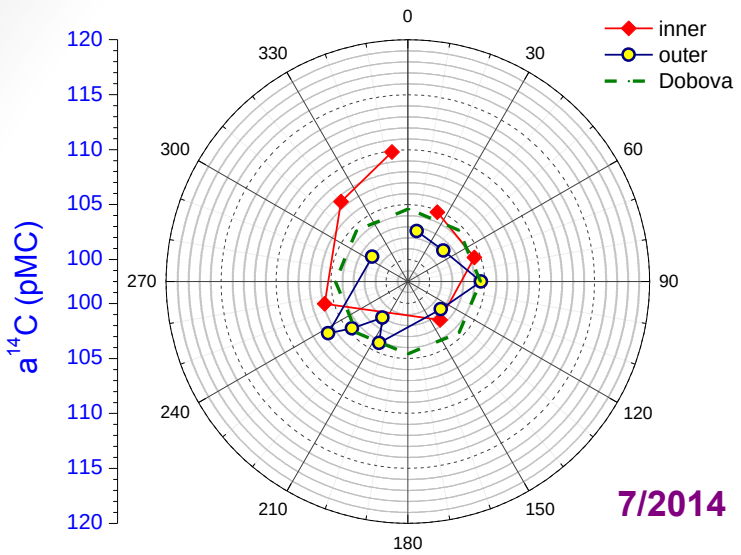
7/2007 9/2007

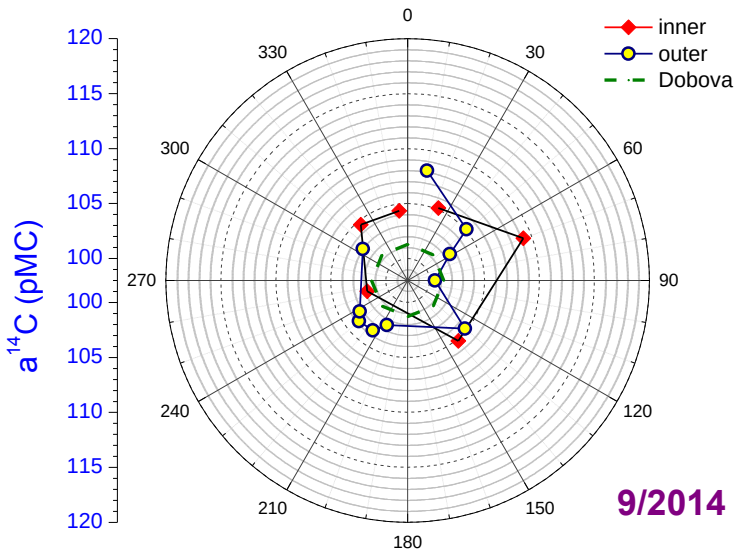
Polarni diagrami aktivnosti ^{14}C bioloških uzoraka – ljetno uzorkovanje nakon proljetnog remonta, 2006, 2009, 2012

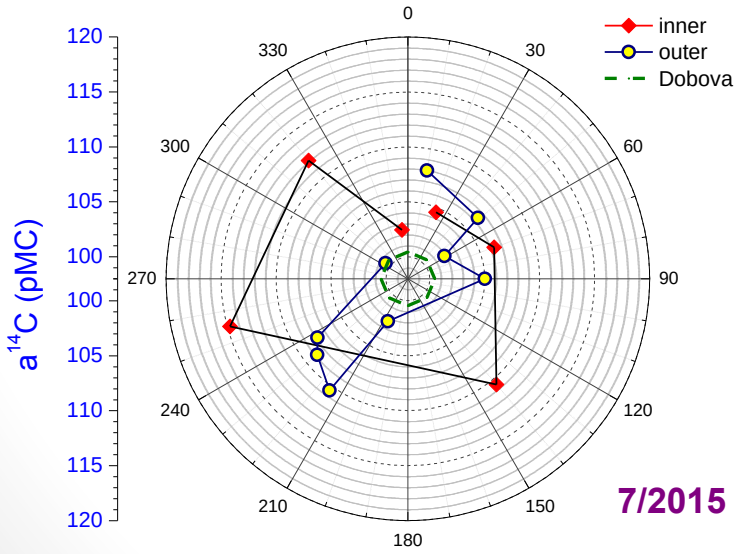










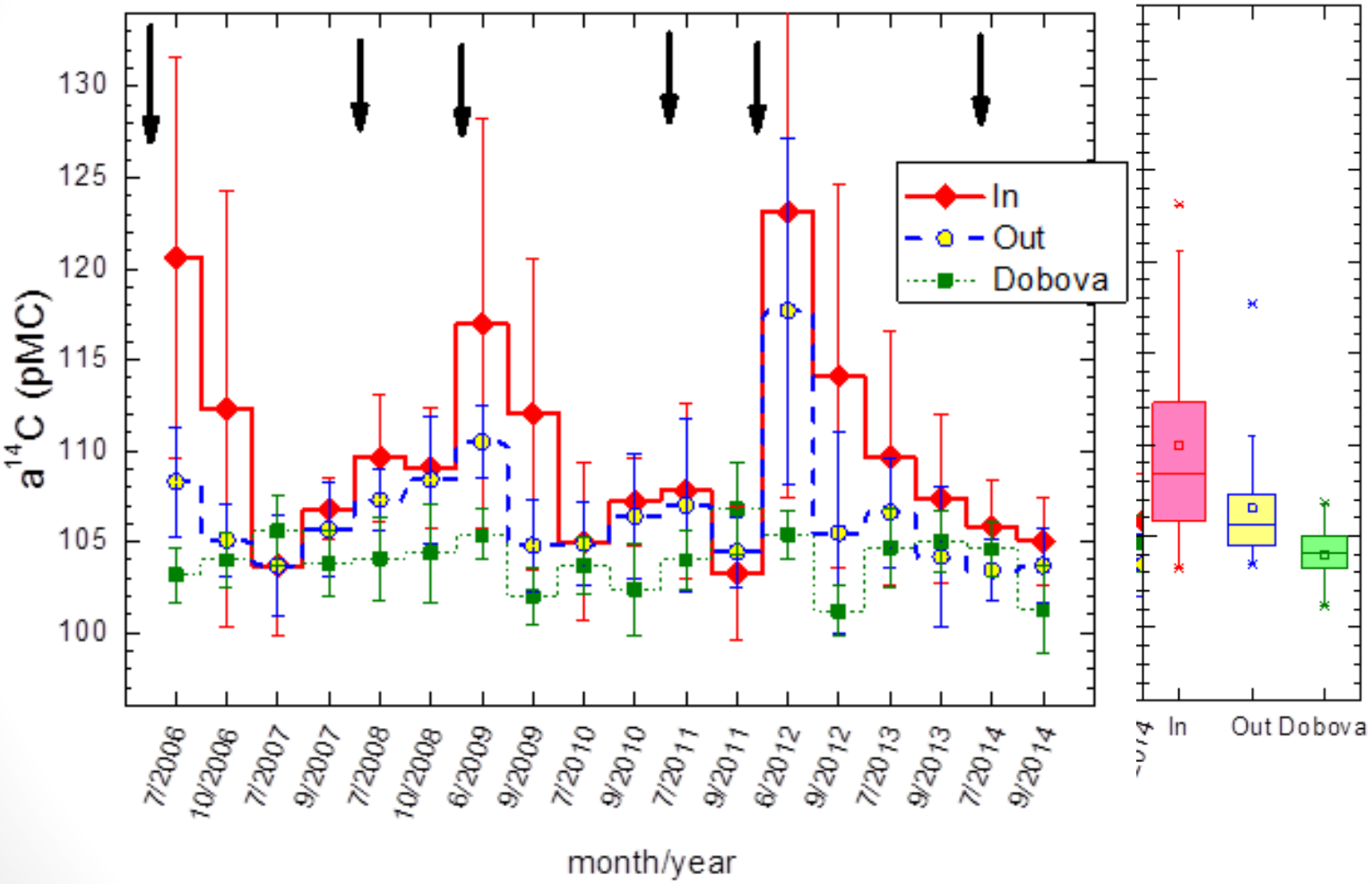


Nakon proljetnog remonta 2015
U atm CO_2 izmjerene su niže ^{14}C aktivnosti nego tijekom prethodnih

Prosječne vrijednosti $a^{14}C_{atm}$ [pMC] u biljkama u unutarnjem i vanjskom krugu i na kontrolnoj točki, 2006.–2014. Osjenčano: nakon remonta.

Datum sakupljanja mjesec/godina	**$a^{14}C$** (pMC) **unutarnji krug**	**$a^{14}C$** (pMC) **vanjski krug**	**$a^{14}C$** (pMC) **kontrolna točka**
07 / 2006	120.6 ± 11.0	108.3 ± 3.0	103.2 ± 1.5
10 / 2006	112.3 ± 12.0	105.1 ± 2.0	104.0 ± 1.5
07 / 2007	103.7 ± 3.9	103.7 ± 2.8	105.6 ± 1.9
09 / 2007	106.8 ± 1.7	105.7 ± 2.6	103.8 ± 1.8
07 / 2008	109.6 ± 3.5	107.3 ± 1.7	104.1 ± 2.3
10 / 2008	109.1 ± 3.3	108.4 ± 3.5	104.4 ± 2.7
06 / 2009	117.0 ± 11.2	110.5 ± 2.0	105.4 ± 1.4
09 / 2009	112.0 ± 8.5	104.8 ± 2.5	102.0 ± 1.6
07 / 2010	105.0 ± 4.3	104.9 ± 2.3	103.7 ± 1.6
09 / 2010	107.2 ± 2.4	106.4 ± 3.4	102.4 ± 2.5
07 / 2011	107.8 ± 4.8	107.0 ± 4.8	104.0 ± 1.6
09 / 2011	103.2 ± 3.6	104.4 ± 1.9	106.8 ± 2.5
06 / 2012	123.1 ± 15.7	117.7 ± 9.5	105.4 ± 1.3
09 / 2012	114.1 ± 10.5	105.5 ± 5.5	101.2 ± 1.4
07 / 2013	109.6 ± 6.9	106.6 ± 3.0	104.7 ± 2.1
09 / 2013	107.4 ± 4.6	104.2 ± 3.8	105.0 ± 1.6
07 / 2014	105.8 ± 2.6	103.4 ± 1.7	104.6 ± 1.6
09 / 2014	105.1 ± 2.4	103.7 ± 2.0	101.3 ± 2.4
srednja vrijednost	**110,0 ± 5,5**	**106,5 ± 3,3**	**104,0 ± 1,5**

Srednje vrijednosti po sezonama



Na istoj lokaciji različiti uzorci

Dobova	$a^{14}C$ [pMC]	σ
Kukuruz	102,9	1,8
Pšenica	103,1	1,8
zob	103,7	1,8

Lokacija D	$a^{14}C$ [pMC]	σ
jabuka	105,2	1,7
Lišće grma	105,8	2,4

Lokacija F	$a^{14}C$ [pMC]	σ
jabuka	102,3	2,1
kukuruz	102,7	2,1

Lokacija J	$a^{14}C$ [pMC]	σ
jabuka	100,6	2,5
Jabuka, druga vrsta	101,5	2,5
Poljsko cvijeće	103,8	2,6

Procjena efektivne doze

Godišnja doza uslijed prisutnosti ^{14}C u hrani:

$$E = e \times a^{14}C \times m \times t$$

t 365 dana

m masa ugljika uneseno dnevno hranom (0,3 kg, ICRP, 1996)

100 kg C godišnje

$a^{14}C$ mjerena aktivnost ^{14}C (Bq/kg C)

e ingestijski dozni koeficijent za ^{14}C (očekivana efektivna doza po jediničnoj aktivnosti ^{14}C **$5{,}8 \times 10^{-10}$ Sv/Bq** (ICRP, 1996)

Pregled prirodnih doza

Ukupna: **1220 μSv,** iz svih prirodnih izvora

Ingestija: **~300 μSv,** najveći doprinos ^{40}K, ^{137}Cs, ^{90}Sr

^{14}C doza : **~15 μSv**

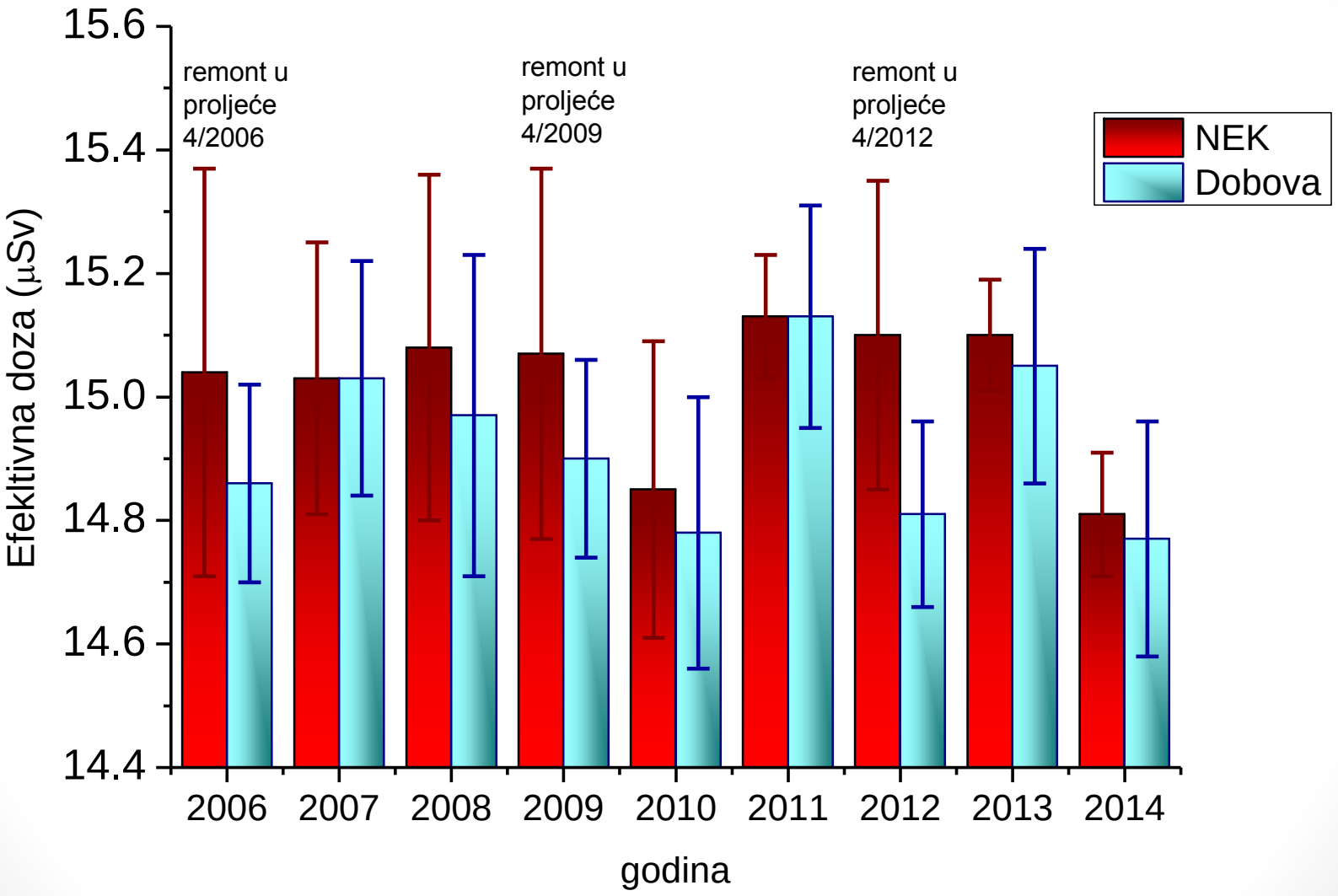
Povećanje ekvivalentne doze ^{14}C u odnosu na prirodnu ^{14}C dozu izmjerenu na kontrolnoj točki (Dobova) i povećanje ukupne doze u odnosu na prirodnu dozu u našim krajevima (1,22 mSv).

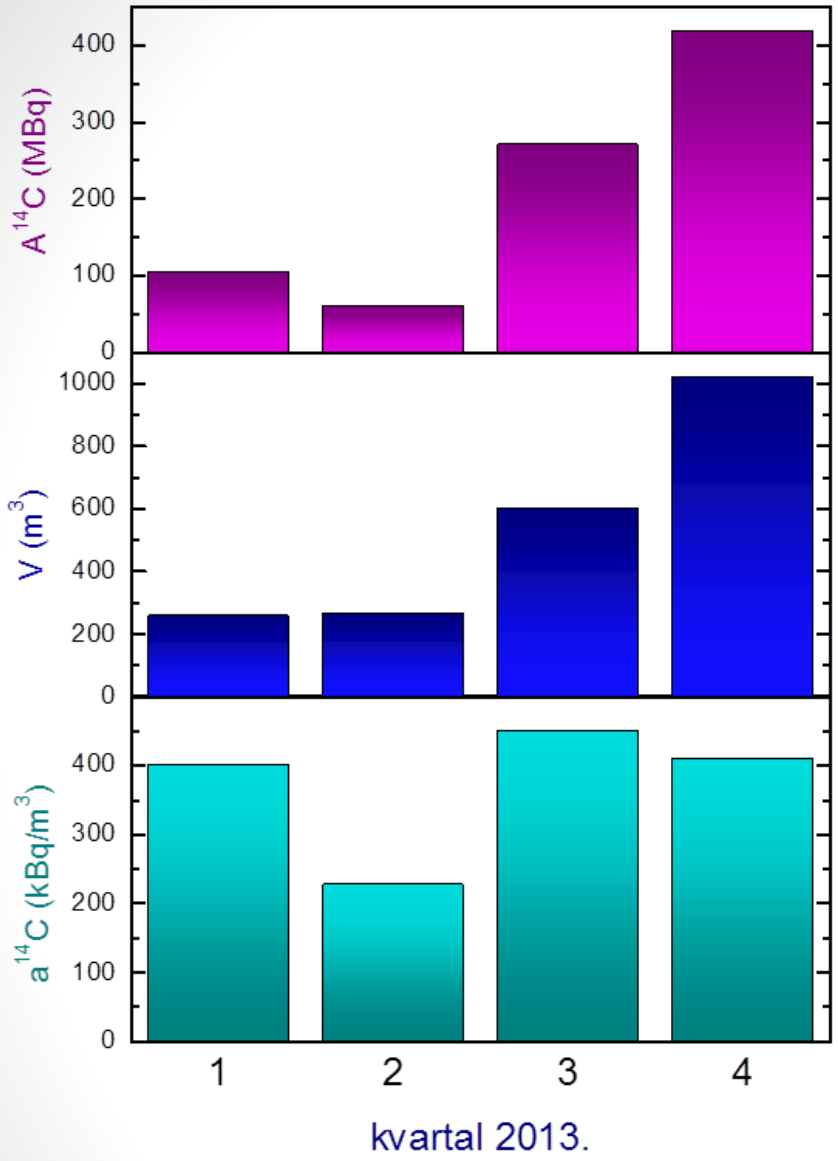
Godina	**a^{14}C NEK *** (pMC)	**a^{14}C Dobova** (pMC)	**Doza ^{14}C NEK** (μSv)	**Doza ^{14}C Dobova** (μSv)	**Povećanje doze ^{14}C** (%)	**Povećanje ukupne doze** (%)
2006	111,6 ± 8,3	103,5 ± 1,1	15,04 ± 0,33	14,86 ± 0,16	**1,29**	**0,0159**
2007	105,0 ± 2,6	104,7 ± 1,3	15,03 ± 0,22	15,03 ± 0,19	**0,04**	**0,0005**
2008	108,8 ± 2,6	104,3 ± 1,8	15,08 ± 0,28	14,97 ± 0,26	**0,71**	**0,0088**
2009	110,8 ± 7,1	103,8 ± 1,1	15,07 ± 0,30	14,90 ± 0,16	**1,11**	**0,0137**
2010	105,8 ± 2,7	103,0 ± 1,5	14,85 ± 0,24	14,78 ± 0,22	**0,45**	**0,0055**
2011	105,6 ± 3,8	105,4 ± 1,5	15,13 ± 0,10	15,13 ± 0,18	**0,03**	**0,0004**
2012	115 ± 10	103,2 ± 1,0	15,10 ± 0,25	14,81 ± 0,15	**1,92**	**0,0233**
2013	106,8 ± 3,5	104,8 ± 1,3	15,10 ± 0,09	15,05 ± 0,19	**0,32**	**0,0039**
2014	104,3 ± 2,2	102,9 ± 1,4	14,81 ± 0,10	14,77 ± 0,19	**0,22**	**0,0027**

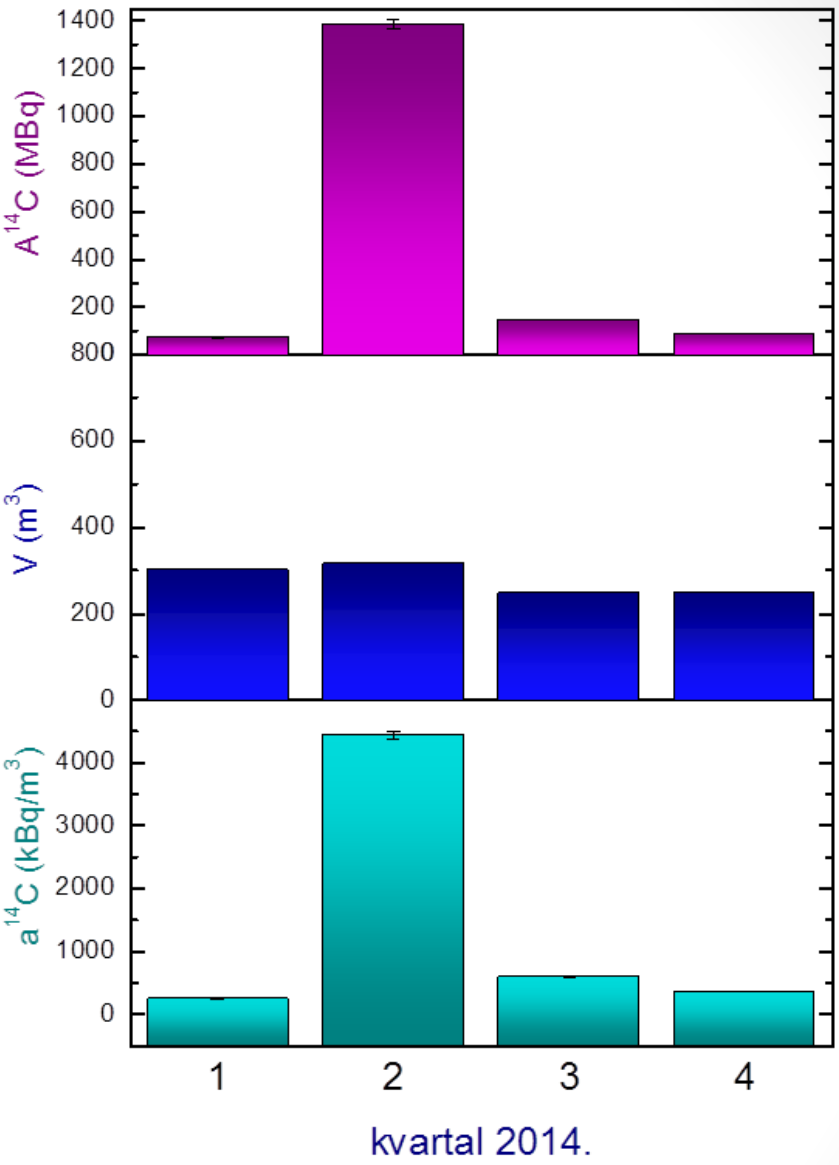
model prehrane za okolicu NEK:
2 mjeseca iz okolice NEK, sve lokacije u prosjeku, ostalih 10 mjeseci iz Dobove

Prosječne vr. 15,02 14,92 μSv
razlika 0 – 0,29 μSv, prosjek 0,10 μSv

Usporedba efektivnih godišnjih doza zbog ingestije, samo ^{14}C



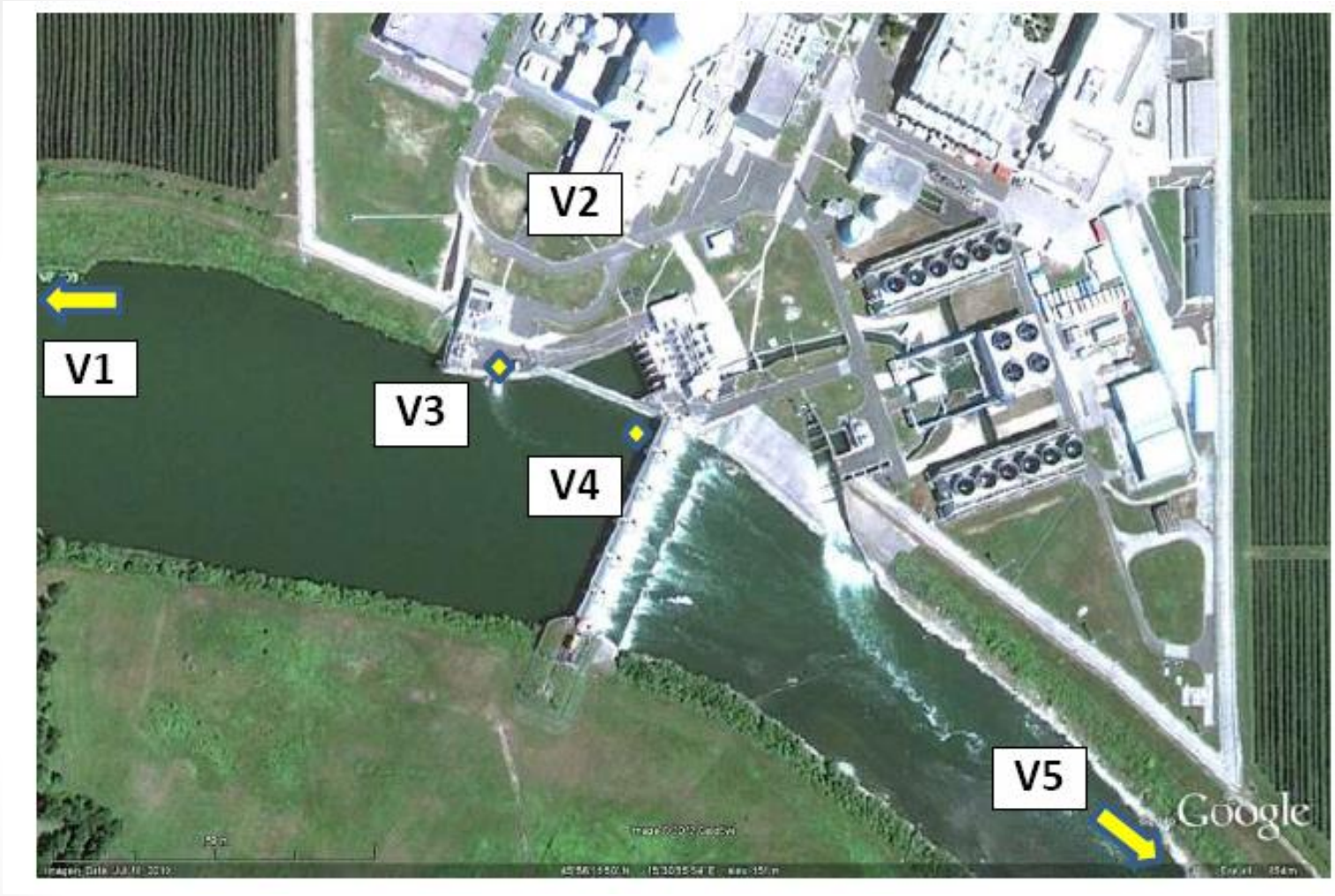




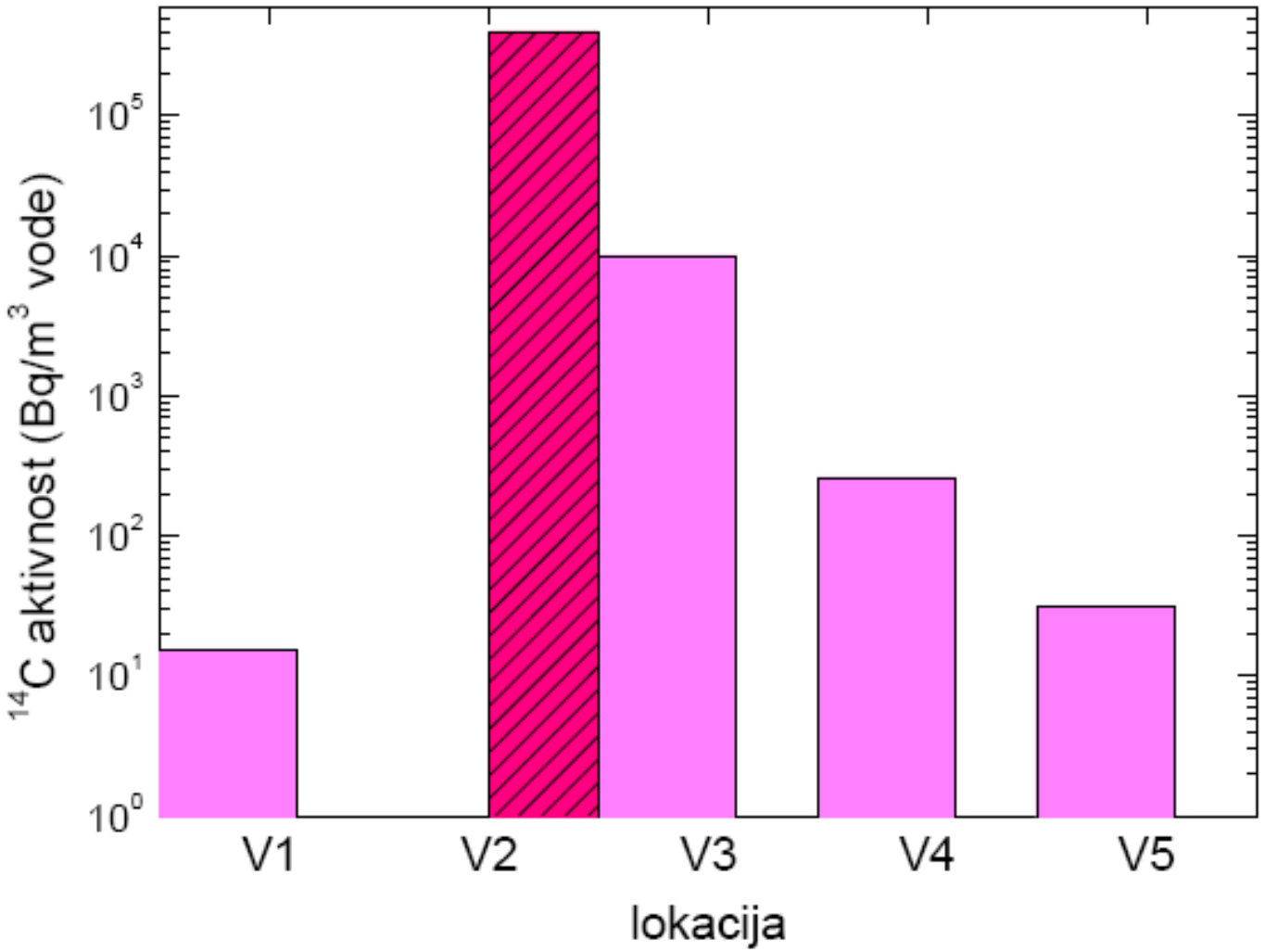
Ukupna godišnja ispuštena aktivnost ^{14}C u tekućim ispustima

2013. - 852 MBq

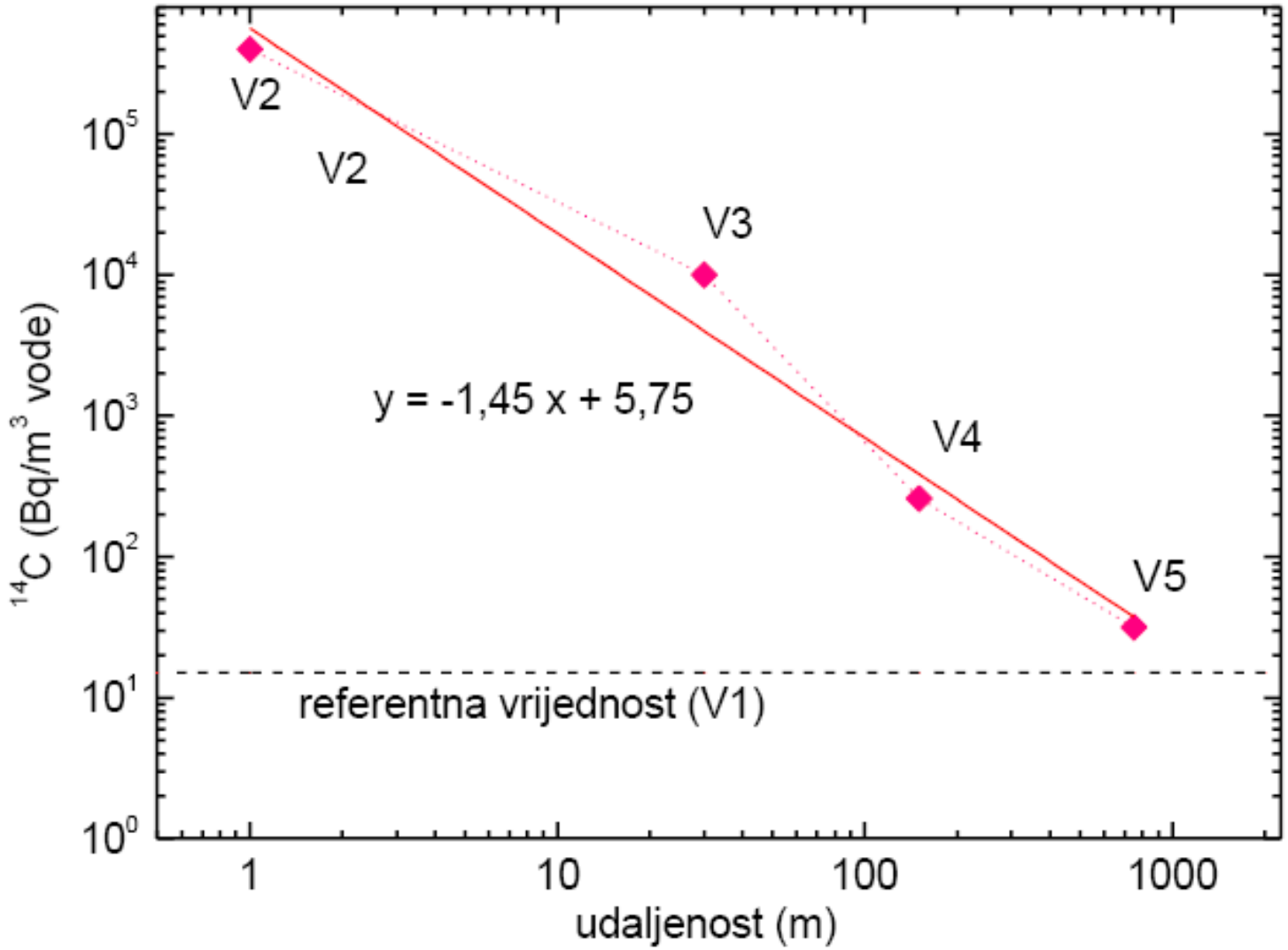
2014. - 1693 MBq (1,7E9 Bq)



28.3.2013. ^{14}C u Savi i WMT


^{14}C aktivnost (Bq/m^3 vode)
10^5
10^4
10^3
10^2
10^1
10^0
V1
V2
V3
V4
V5
lokacija

Procjena udaljenosti na kojoj se ^{14}C aktivnost rijeke vrati na "prirodnu" – 1400 m



Riba (2014, jednokratno)

Oznaka uzorka	Naziv uzorka	$a^{14}C$ (pMC)	$a^{14}C$ (Bq/kgC)	$A_s{}^{14}C$ (Bq/kg suhe tvari) [1]	$A_r{}^{14}C$ (Bq/kg ribe) [2]
Z-5473 B1191	**Riba – klen iz Save, Jesenice, JE06-14R1**	98,7 ± 0,8	223,0 ± 1,8	52,10	12,17
Z-5474 B1192	**Riba – deverika iz Save, Jesenice, JE06-14R2**	95,9 ± 0,8	216,7 ± 1,8	54,86	13,89

NEK riba (2014) 1 kgFW = 72 % voda + 28 % DW

(IAEA TRS472: 72-75% vode)

karbonizacija app. 25% od suhe tvari (IAEA TRS472: 40 – 47%)

➔ **B = 12,2 (13,9) Bq/kgFW / 11.3 E-3 Bq/L = 1070 (1230) L/kg**

Neki drugi rezultati monitoringa ^{14}C u okolišu nuklearnih elektrana

Cernavoda – CANDU reaktor 2 × 700 MWe

fish ^{14}C spec activity 327 ± 26 (range 240 – 430) Bq/kgC (144 pMC)

vegetable average 338 ± 27 (range 240 – 470) Bq/kgC (150 pMC)

no significant difference between different types of vegetables

background level 246 Bq/kgC (109 pMC)

maximum ^{14}C in grass at 400 m 308 ± 5 Bq/kgC (136 pMC)

From: **Popoaca et al, JEPE 2014; Olarin 2001**

Sellafield – nuclear fell reprocessing plant

aquatic ^{14}C discharges are almost exclusively in the form of DIC

liquid marine discharges (as inorganic C incorporated into DIC) to the Irish Sea,

1984 – 1993 average 1.78 TBq/yr

1994 8,17 TBq/yr

1994 – 2013 average 8.13 TBq/yr

NEK liquid discharges 2013 0.8 GBq, 2014 1.7 GBq

(3-4 reda veličine manje ispuštene ^{14}C aktivnosti!!)

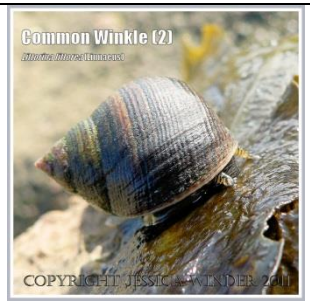
measured ^{14}C in seawead samples (annualy collected)

range 310 (1992) – 1200 (1995, 1996, 1998) Bq/kgC (137 – 530 pMC),

correlated with discharged ^{14}C activity (1.5 – 12 TBq)

mussel shell ^{14}C activity responds in accordance with the discharge activity during the growth period

From: Cook et al (2004, JRNC); Tierney et al (2016, J Env rad)

		
mussel – dagnja	winkle – nanara, pužić	cockle – (bivalve) srčanka

^{14}C activity in whole shells follows the trends

mussel 917 Bq/kgC (dagnja, feed by phytoplancton that is feeded by DIC exclusively) → **winkles 640 Bq/kgC** (can use atmospheric carbon) → **cockles 495 Bq/kgC** (live in sediment at 5-10 cm depth, may use organic matter of lower ^{14}C act from sediment to shell formation), that reflects the feeding habits of shells

Povinec, Radiocarbon 2015, ARI 2008, JenvRad2009

- impact of NPP close to the statistical limit, negligible contribution to the radiation dose delivered to local inhabitants (by app. 3 order of magnitude below dose limit of 1 mSv/yr)

Yim, 2006

- individual effective dose rates (food production and consumption patter for rural setting) 4 μSv/yr (BWR) and 2.3 μSv/yr (PWR)
- this corresponds to the fatal cancer level in the order of 10^{-7} per year, this is 3 orders of magnitude lower than the risk from natural background radiation (10^{-4} /yr) and is a very small fraction of regulatory dose limit for the public

S. Roussel-Debet, J Env Rad 2006

- 10 years of measurement of ^{14}C around French nuclear power plant sites
- zone influenced and zones not influenced by gaseous releases
- discharges have a very slight impact on the ^{14}C level – about 3 Bq/kgC increase in the influenced area, beckground level 242 ± 6 Bq/kgC
- near-negligible increase in dose, on average **< 0.1 μSv/yr**
- $\delta^{13}C$ values about -27 ‰ in both influenced and non-inluenced areas
- all models of ^{14}C transfer in the environment are based on the principle of isotopic equilibrium – specific activity of the carbon (expressed in Bq/kgC) in plants is the same as in the atmosphere and this model is valid for all trophic levels
- the effective annual dose – influenced zone 1.41 10^{-5} Sv (14.1 μSv/yr), non-influenced zone – 1.39 10^{-5} Sv (13.9 μSv/yr), a negligible increase of 0.18 μSv/yr (1.3 %) can be attributed to the effect of gaseous releases